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SURFACE BLACKENING PROCESS FOR STEELS

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This invention relates to a process for blackening the surfaces of articles made of steel, and more particularly stainless steel.

The blackening of articles made of steel may be required in order to provide an attractive finish, or for technical reasons. As an example of the latter, the outer portion of the bodies of alternating current data transmission devices, known as synchros, are made of stainless steel. The synchros become heated in use and if the outer part of the body is given a dull black finish radiation is increased so that the instruments may be operated at a higher electrical rating, whilst still keeping within specified limits of temperature. For certain parts of optical apparatus a dull black finish is essential.

It is known that stainless steel articles may be blackened by immersing them for a period of time in a molten bath of sodium dichromate. The bath is maintained at a temperature between about 320° C. and 500° C., it is usually held slightly below the temperature of decomposition, which varies according to the composition of the bath. The dichromate contains considerable quantities of available oxygen and if foreign organic matter is accidentally introduced into the bath, as for example, in the shape of materials clinging to the articles to be blackened, then the dichromate reacts violently with the foreign matter. The higher temperature achieved locally causes decomposition and this may spread throughout the whole bath, thus producing an explosion.

In heating the bath of dichromate it is difficult to ensure that the heating over the whole surface is absolutely even. If the heating is uneven then local overheating with resulting decomposition may easily occur. Furthermore, if the articles to be blackened should be wet, or if small amounts of water should be present in cavities such as tapped holes, then violent sputtering and splashing of the molten salt may occur. The risks involved in using such baths are very substantial and serious accidents have occurred.

Methods have also been described in which the dichromate is applied to the surface in water solution, subsequently dried and then heated to the required temperature. The temperature and concentration of the dichromate solution should be closely controlled to obtain large spangled crystals on the surface of the metal pieces or articles. It is difficult to control the concentration of a solution at elevated temperatures and the health hazard of spray from dichromate solutions is well known. Further, it is difficult to obtain a sufficient thickness of dichromate on the surface in a single application.

An object of the present invention is to provide a medium which may be applied to the surface in the cold condition and in a single coating.

In investigating the effects of other compounds of chromium it has been found that partial reduction of the dichromate is beneficial. This reduction is carried out in such a manner as to produce chromium chromate $2Cr_2O.CrO_3$. This substance is formed by the action of reducing agents, for example, sulphur dioxide, sodium metabisulphite, alcohol, etc. on a hot aqueous dichromate solution and the product is gelatinous. The advantages of this partial reduction of the dichromate are, firstly, that a thinner coating is adequate to produce a satisfactory finish and secondly that the medium is

more easily applied to the articles as the film need not be so thick. The medium need not be used hot and the growth of large crystals during storage does not occur. The gelatinous compound tends to deposit fine brown powder on storage but this is readily suspended in the solution by shaking or stirring before use. It is chemically similar to the gelatinous compound and has no adverse effect on the quality of the final black film on the steel article. A coating medium of this type may be produced as follows:

Example A

Sulphur dioxide is bubbled through a solution of 100 grams of sodium dichromate in 150 ml. of water at 80° C. until absorption ceases. During the reaction heat is involved and it is necessary to cool the vessel to prevent the temperature from rising above 100° C. The solution is then boiled to drive off excess sulphur dioxide and allowed to cool. To this solution is added a further solution containing 150 gms. of sodium dichromate, 5 gms. of sodium alginate and 1 gm. of surface active agent dissolved in 100 ml. of water. This solution is applied cold.

Whereas a solution of dichromate must be applied so as to leave a one-twentieth of an inch of solid dichromate on the surface after preliminary drying, the medium described in Example A gives satisfactory results when the thickness of the gel on the surface is only one-hundredth of an inch. Owing to the tenacious nature of the gel no special care is necessary in its application. It is sufficient to brush the surface lightly with the gel, a single application being sufficient. With this medium it is not necessary to dry the coating before it is heated to the temperature at which the blackening reaction occurs nor is it necessary to obtain a particular crystal formation.

While the coating obtained with this solution is satisfactory, a somewhat more uniform finish is produced by coating with a medium prepared by the method to be described in connection with the formula of Example B.

From an investigation of the nature of the black coating it seems likely that it consists of a compound of chromium and iron, probably similar to the chromite $FeO.Cr_2O_3$. It has been found that the addition of iron salts to the coating medium improves the finish and provides a more uniform black. Various iron salts may be used but ferrous sulphate is preferred since it also produces the partial reduction of the dichromate previously described and it is readily available at low cost. A coating medium containing ferrous sulphate is:

Example B

	Parts by weight
Sodium dichromate, dihydrate	500
Ferrous sulphate, heptahydrate	170
Sodium alginate	10
Surface active agent	1
Water to make	1000

The medium is prepared by dissolving the sodium dichromate in hot water (about 80° C.) adding the ferrous sulphate and boiling for five minutes. The sodium alginate and surface active agent are added and the solution is allowed to cool.

This medium is more easily applied than any of those previously described. It may be applied cold and a very thin coating is sufficient to produce a satisfactory black finish.

Furthermore, the coating has very little tendency to "spread" on heating to the reaction temperature and it is therefore possible to produce selective blackening

of the article to be treated by applying the coating to localised parts of its surface.

After the articles have been coated by any of the methods herein described, heat is applied by means of a flame, by placing the articles in a temperature-controlled oven or furnace, or by radiant heat. The final temperature is not critical but should be higher than 320° C. Heating up to red heat will not have any adverse effect on the coating but a preferred temperature is 450° C. The time during which heating is continued depends upon the rate at which the temperature of the article rises and upon the maximum temperature. A satisfactory finish may be obtained on some articles by treatment in an oven held at 450° C. for as little as five minutes, but the preferred treatment time for average articles is 20 minutes. The process has been found completely safe in operation.

After heating the excess dichromate and oxides of chromium are removed by washing in running water.

The black finish normally obtained by this process is dull. It is very durable and is integral with the surface. A highly polished decorative surface may be obtained by buffing, using one of the usual fine polishing compounds. The degree of polish obtained is to a great extent influenced by the smoothness of the surface prior to blackening. When a durable matt black finish is required it is desirable that the surface of the article should be rendered matt prior to treatment, for example, by fine sand or sheet blasting.

A coating medium containing ferrous sulphate was defined in Example B. The addition of salts of metals other than iron has been investigated and it is found that a number of metallic salts will influence the nature of the final surface. For example, copper sulphate causes mottling of the surface whilst manganese sulphate produces a softer film.

It has been found that by the use of the processes herein described a satisfactory black finish may be produced on a wide range of steels, even if they do not contain chromium. For example, equally good coatings have been produced on an austenitic stainless steel containing 18% chromium, and 8% nickel, a steel containing 1% chromium, 25% nickel and small amounts of cobalt, tungsten, vanadium and silicon; and a mild steel having a low carbon content and substantially free from alloying elements.

We claim:

1. A process for coating the surface of articles made of steel with an integral black coating of oxides of chromium and iron in which the articles are coated in the cold state with a coating medium comprising an aqueous gel made by partially reducing dichromate solution and the temperature is subsequently raised to above 320° C.

2. A process as claimed in claim 1 in which the coating medium is a solution of dichromate in a gel of reduced dichromate.

3. A process as claimed in claim 1 in which the coating medium contains a soluble salt of iron.

4. A process as claimed in claim 3 in which ferrous sulphate is used to produce the partial reduction of the dichromate solution.

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