METHOD OF BLACKENING FERROUS METAL SURFACES

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ABSTRACT

Disclosed is a method of forming a corrosion resistant and decorative black coating on a ferrous metal surface. The method involves contacting the ferrous workpiece with an aqueous slightly acidic solution containing the nitrate ion and a soluble nitrogen containing cation. Preferably, the solution is obtained by dissolving both ammonium nitrate and a neutral nitrate salt in water and maintaining a pH of between 4.0 and 6.8.

10 Claims, No Drawings
METHOD OF BLACKENING FERROUS METAL SURFACES

This application is a continuation-in-part of U.S. Serial No. 359,146 filed May 10, 1973, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the treatment of ferrous metal surfaces to form a corrosion resistant coating thereon. More particularly, it relates to the formation of such a corrosion resistant coating which is also a decorative black coating.

Numerous patents and publications disclose methods for obtaining a black oxide coating on metal surfaces. The two commercial methods involve either contacting the workpiece with an aqueous solution of a strong alkali and an oxidizing agent, or contacting the workpiece with a molten salt solution containing a strong oxidizing agent.

Examples of systems relying on a strong alkali aqueous solution are demonstrated in U.S. Pat. Nos. 2,431,728; 2,750,301; 2,817,610; 3,142,592; 3,447,974; and 3,279,957, the disclosures of which are incorporated herein by reference. The last mentioned patent is representative of the current state of the art of the strong alkali systems. The treating solution contains between approximately 25% and 50% sodium hydroxide. The temperature of the treating solution, in order to obtain a satisfactory black oxide coating, should be in the neighborhood of 300°F. While such solutions do produce acceptable coatings, they involve a number of difficulties. The high pH of the alkali bath necessitates special safety precautions. Furthermore, the high concentration of alkali ingredients complicates waste disposal problems. Dragout from the bath to the subsequent rinse also results in an undesirable change in the pH of the rinsing water. This effect may require the bath operator to adjust the pH of rinse water before discarding it. Finally, the cost of maintaining the relatively high temperatures in the neighborhood of 300°F in the treating bath contributes to increased cost in the process. It would, therefore, be desirable to develop a process which avoids the foregoing shortcomings.

The molten salt baths above-referred-to are exemplified by U.S. Pat. Nos. 2,370,959; 2,394,899; 2,431,986; and 3,540,942; the contents of which are incorporated herein by reference. The molten salt process requires extremely high temperatures for its effectiveness. Temperatures range from between 600° and 1500°F and higher. A process operating at much more moderate temperatures in the neighborhood of 200°F would avoid the expensive heating costs and would also avoid the complications of working with molten salt materials.

The disadvantages of both of these processes are overcome by the method of our invention.

The method of our invention should not be confused with prior experimental work concerned with fertilizer solutions. Aqueous fertilizer solutions are often shipped containing 40-60 weight % NH₄NO₃ and 20 weight % NH₃. A considerable amount of experimental effort has been directed toward trying to determine how to prevent excessive corrosion resulting from the chemical action of this ammonium nitrate solution itself upon the tanks for containers or pipelines through which it flows. See, for example, U.S. Pat. Nos. 2,366,796; 3,617,240; Corrosion Science, Volume 10, pages 745 to 759, 1970; Corrosion, Volume 18, No. 1, Jan., 1962; Journal of the Electrochemical Society, Nov., 1964, pages 1211 to 1215; and Corrosion Science, Volume 8, 1968, pages 561 to 572. These patentees and authors were concerned with the failure of shipping tanks and pipes when in contact with ammonium nitrate as a result of stress corrosion cracking. This specific concern of the fertilizer industry is unrelated to metal treatment for decorative and anti-corrosion purposes.

SUMMARY OF THE INVENTION

Our invention is based upon the discovery that a slightly acidic aqueous solution containing nitrate ion and a soluble nitrogen containing cation selected from the group consisting of ammonium, pyridinium and their derivatives will effect a corrosion resistant and decorative black coating on predominantly iron workpieces. The treating bath may additionally include accelerators to speed up the reaction, surfactants to inhibit film and scum formation, and scavenger compounds which operate to remove undesirable ions from the solution. Desirably, the workpiece is first cleaned in a conventional alkaline cleaning bath optionally pickled and then contacted with the treating bath of our invention for a period of between 30 seconds and 2 hours under slight agitation. The pH of the bath will be in the range of between 4.0 and 6.8.

DETAILED DESCRIPTION OF THE INVENTION

The nitrate ion may be supplied to the treating bath from any suitable source. While nitrate ion concentrations in excess of 0.01 weight % have been found effective to some extent, the preferred concentration range is between 0.15 and 20.5% and the most preferred range is between 0.25 and 15.0%. At higher percentages, the quality of the coating decreases and at lower concentrations the corresponding temperature and treating time requirements become undesirably long.

The nitrogen containing cation of the present invention may be supplied from any suitable source. Suitable nitrogen cations may be selected from ammonium, pyridinium and derivatives thereof. The major requirements of the compound serving as the cation source are that it be appreciably soluble in the solution and that it not contribute to undesirable side reactions. While the most preferred nitrogen cation is ammonium, substituted ammonium ions have also been found effective to produce the desired coating. Such ions have the general formula:

\[ \text{R}_1 \text{R}_2\text{N}^- + \text{H}^+ \]

\[ \text{R}_1, \text{R}_2, \text{and R}_3 \text{ may be independently selected from hydrogen, alkyl, ary1, substituted alkyl and substituted ary1. The substituted radicals should not contain acid substituents which would yield a pH of less than about 4 when the cationic nitrogen containing compound is dissolved in water. Suitable substituents include, for example — OH, >C=O, —NH}_2. \text{In general, solubility may be a problem where the nitrogen comprises less than about 1.8 weight % of the nitrogen containing cation unless suitable solubilizing substituents are employed. Aniline, N-ethyl aniline and triethanolamine have been} \]
found particularly effective cation sources for producing the desired coating. It is understood that multiple amines such as di- and tri- amines are also included within the invention as equivalents of the above formula. Additionally, the above formula may also encompass cycloaliphatic amines wherein $R_1$ and $R_2$ comprise a single aliphatic group forming a ring structure with the nitrogen atom such as piperidine.

As mentioned, it has further been found that pyridinium, an aromatic nitrogen cation, and its derivatives are also effective for producing the desired black oxide coating. Such compounds have the formula:

\[
\begin{align*}
R_1 & \quad H^+ \\
R_2 & \quad N \\
R_3 & \quad (\text{Substituent}) \\
R_4 & \quad (\text{Substituent})
\end{align*}
\]

wherein $R_1$ through $R_4$ may be independently selected from hydrogen, alkyl, aryl, substituted alkyl, and substituted aryl. Additionally, the above formula may also encompass compounds where adjacent R groups are part of a fused benzene ring or substituted benzene ring (such as occur in the compound quinoline). It is understood that aromatic nitrogen compounds containing more than one nitrogen atom per aromatic ring, such as pyrimidine or its derivatives are also included within the invention as equivalent of the above formula. In general, the nitrogen should comprise at least about 1.8 weight % of the cation to help avoid solubility problems. Again, the appropriate limitations on the derivatives are that they must be soluble in the bath to an appreciable extent and they must not contain any substituent which would interfere by causing undesirable side reactions. The preferred component of this type is the unsubstituted pyridinium ion.

The precise concentration of the cationic nitrogen containing compound in the bath is not critical so long as the pH requirements stated hereafter are met. Desirably, the mole ratio of nitrogen in the cationic nitrogen containing compound to total nitrate in the solution will be in excess of 10:1. Preferably, the ratio is between .001 and 1:1. It should be appreciated, however, that one may conveniently add an excess of the nitrogen compound in order to increase the pH of the solution after the addition of the nitrate compound. On the other hand, where the cationic nitrogen containing compound is added in the form of the nitrate itself, the pH will normally be within the desired range, and there will be no need to do any pH adjusting. A mole ratio of less than 1 may be obtained by adding a portion of the nitrate as a neutral salt such as sodium, potassium, magnesium calcium or the like. Good results have been obtained for the widest variety of steel alloys when the ratio is from 0.01-0.5 to 1.

The pH of the slightly acidic treating bath should be adjusted to a value of between about 4.0 and 6.8. Preferably, the bath should have a pH of between 4.5 and 6.5 and most preferably between 5.0 and 6.0. The use of more acidic baths results in an undesired extent of pickling whereas baths of a higher pH result in no coatings or lengthy coating times and, in the case of very simple nitrogen compounds, may result in the evolution of ammonia or similar nitrogen containing gases if the pH is adjusted to about 7 or above.

The workpiece should be maintained in contact with the treating solution for a time sufficient to produce the desired black oxide coating. Application may be either by flooding or immersion techniques. Typically, the desired contact time will vary between 30 seconds and 2 hours and preferably between 5 and 30 minutes depending upon the temperature of the solution and concentration of the reactive ingredients.

The temperature of the treating solution should be between 140°F and the boiling point of the solution. Preferably, the temperature will be between 160°F and 215°F and most preferably between 180°F and 210°F. Higher temperatures are undesirable because of changes in the solution due to boiling and the need for additional heat input, whereas lower temperatures tend to result in a poorer quality coating and an increased rate of scum formation. Where the active ingredients are provided in the form of ammonium nitrate, a 1 weight % solution of ammonium nitrate will require a temperature of in the range of 200°F to 210°F whereas a 10 weight % solution will require a temperature of approximately 165°F in order to produce the desired coating on ordinary steel after 15 minutes immersion.

Control problems and side reactions become increasingly significant as the NH₄NO₃ concentration goes above 5% at a temperature of 200°F and as concentration goes above 30% at a temperature of 160°F.

It is essential that the workpiece be thoroughly cleaned in accordance with conventional metal cleaning procedures known in the art. Typically, a phosphate containing alkaline cleaning bath will be suitable. Improper cleaning will result in spotty and streaked coatings which are not acceptable from either a corrosion or an esthetic viewpoint. If desired, the workpiece may be pickled prior to treatment in accordance with the invention. When the workpiece is treated via immersion in our bath, it is preferred that slight agitation be employed to insure uniformity of the resulting coating.

A variety of additional components have been found desirable for various reasons. Accelerating compounds, primarily those acting as oxidizing agents, have been found useful. Any oxidizing agent normally employed in metal treating solutions such as nitrite, chlorate, bromate and peroxide may be employed. The concentration is desirably maintained at low levels depending on the particular agent employed, generally less than 1 weight %. A preferred concentration range for the nitrite ion is from 0.0005 to 0.01%. In an active bath through which ferrous metal workpieces are being passed on a regular basis or where the bath has a high nitrate concentration, a nitrite concentration within the above range will normally be present as a result of the reduction of the nitrate ion. On the other hand, in either a fresh or inactive low nitrate bath, the nitrite concentration would decrease essentially to 0. In the preferred embodiment of this invention, additional nitrite ion should be added during these startup periods so that nitrite ion will continuously be present while workpieces are being processed. While it is not entirely understood, it has been found that a failure to include a small amount of nitrite ion during these startup stages may result in a bath which will neither coat at all or will coat unpredictably from one time to the next. Chlorate may also be used as an advantageous additional component. It will be desirably included in amounts up to 1 weight % and preferably between .005 and .07 weight %.
including too much chlorate will result in a blue cast of the coating or in coatings which are powdery and therefore undesirable. A certain accelerating effect may also be obtained by bubbling air or other oxygen containing gas through the bath while treating the metal workpieces.

Supplemental components may be added to accomplish various purposes. Surfactants may be added to suspend or disperse the insoluble by-products and to inhibit the rate of formation of film and scum on the surface of the bath. Film and scum are, of course, undesirable because components thereof may adhere to the workpiece as it is withdrawn from the bath. The surfactants found most preferred are those of the non-ionic variety such as the nonyl phenol compounds because these tend to interfere least with reactive components and mechanisms of the bath. Suitable non-ionic surfactants are well-known in the art and need not be here recited.

An additive which has been found particularly useful in our bath is ferric nitrate. Ferric nitrate may act as a scavenger in order to regenerate a bath which has become poisoned by the presence of extraneous ions. It has been found that very small quantities of phosphate ions which tend to be carried over from the prior cleaning step will inactivate the bath. The addition of ferric nitrate initiates a series of reactions which precipitate the phosphate ion from the bath and, in effect, operates to regenerate the activity of the bath, renewing its activity toward the formation of the black oxide coating.

Ferrous metal workpieces which may be treated in the bath of our invention are those which consist predominantly of iron. Common metal compositions and alloys containing other metals such as chromium, nickel, magnesium, vanadium, lead as well as compositions including common amounts of phosphorous, sulfur and carbon may be treated.

The corrosion resistance and physical appearance of the black oxide coating obtained by our technique equal that obtained by the conventional alkali treating process. The conventional processes often employ a subsequent treatment with a rust-preventive oil such as those referred to at page 565 et seq. of Metals Handbook, Vol. 2, A.S.M. (8th ed.) 1964. The purpose of this treatment is to improve both appearance and corrosion resistance. Coatings obtained by our process exhibit the same improvements when thus post-treated. One suitable solvent-based system contains approximately ten parts of Alox 2028, a proprietary rust preventive chemical manufactured by Alox Corporation and having a typical acid number of between 3 and 5, a saponification number of between 61 and 69, specific gravity at 75°F of approximately .95, a flash point of approximately 330°F and a melting point of approximately 95°F. The purpose of this treatment is to improve both appearance and corrosion resistance. Coatings obtained by our process exhibit the same improvements when thus post-treated.

One suitable solvent-based system contains approximately ten parts of Alox 2028, a proprietary rust preventive chemical manufactured by Alox Corporation and having a typical acid number of between 3 and 5, a saponification number of between 61 and 69, specific gravity at 75°F of approximately .95, a flash point of approximately 330°F and a melting point of approximately 95°F. This active ingredient may be dissolved in a conventional mineral spirits solvent to provide an effective rust preventive oil. An oil and water emulsion may be prepared by adding Alox 575, a proprietary product of Alox Corporation, having an acid number of approximately 1.02, a pour point of about 80°F and a flash point of about 425°F, about 25 parts by weight, to a balance of a mixture of a high viscosity aromatic oil and a sulfonated hydrocarbon emulsifier which are conventional in the art. Thus, in the most preferred embodiment of this invention, additional anti-corrosive and esthetic properties will be imparted to the workpiece by a final treatment with a rust-preventive oil.

In the most preferred overall embodiment of our invention, the ferrous metal article is first carefully cleaned and water-washed, then contacted with the treating bath of our invention, water-washed, and then subjected to further anticorrosive treatment by contact with a rust-preventive oil.

The following examples demonstrate the utility of our invention:

EXAMPLE 1

Three inch by 5 inch cold-rolled steel (SAE 1010) test panels were flat polished on one side and cleaned so as to be free from grease and oil and surface oxides. They were then immersed in a 0.80% ammonium nitrate solution prepared by dissolving 30 grams of commercial grade ammonium nitrate in one gallon of water. The solution also contains 0.028% sodium chlorate obtained by dissolving 2 milliliters of a 40% sodium chlorate solution in the gallon of water. The solution was maintained at a temperature of 205°F and the contact time was 15 minutes. At the end of this time, a black oxide coating was observed on the metal surface. The workpiece was then rinsed in water and dried by means of a compressed air jet. For comparison purposes, a panel of the same type was coated in a conventional alkaline oxidizing bath containing approximately 80% sodium hydroxide, 15% sodium nitrate and 5% sodium nitrite dissolved in water at a concentration of about 7 pounds per gallon for 15 minutes at 285°F. Panels treated by each of the processes were then spotted with a drop of 5% oxalic acid solution. This test is one employed in accordance with military specifications in order to determine the quality of the coating. If the spot turns a deep black after 5 minutes, then the coating is satisfactory, whereas if it turns a light gray, it is unsatisfactory. After 5 minutes had elapsed, both spots were rinsed and the panels were again air dried and the color of the spots compared. Both spots were a deep black indicating both had a satisfactory black oxide coating.

EXAMPLE 2

Additional panels were treated in the bath of Example 1 and they were subsequently treated with the solvent based rust-preventive oil above-referred-to for several seconds and allowed to drain. Both sets of panels were then subjected to salt spray corrosion testing in accordance with ASTM B-117. After 72 hours in 5% salt fog, the amount of rust formed on the panels treated in the ammonium nitrate-sodium chlorate bath was equivalent to that formed on the panels coated in the conventional alkaline oxidizing bath.

EXAMPLE 3

A number of threaded steel bolts, hexagonal nuts and spark plug shells (extruded from SAE 1105 steel) were treated in accordance with the procedure of Example 2. Again, both sets of parts were deep black in color and were virtually indistinguishable.

EXAMPLE 4

Numerous baths were prepared containing from between .37 and 23.6 weight % ammonium nitrate. All were effective in producing the black oxide coating on the ferrous metal workpieces of Example 3. Baths were prepared both with and without sodium nitrite and with
nitrite concentrations varying between 13 and 135 parts per million. All were found effective in producing the black oxide coating; however, those solutions containing nitrite did so more quickly and with more reliability. Various baths were prepared including various other accelerators and supplemental ingredients in order to determine their effect on the bath activity. The results obtained verified the scope of the invention as earlier described. Temperatures employed varied from 180°F to 212°F. While the most desirable results were obtained at the higher temperatures, the lower temperatures affected acceptable coatings but a longer contact time was required. The black color of the plug shells was comparable in every way to those treated in a conventional alkaline oxidizing bath.

**EXAMPLE 5**

Twenty ml's of concentrated HNO₃ containing 15.8 grams of HNO₂ were dissolved in one gallon of water. 47.4 grams of triethanolamine were added until a pH of 5.5 was reached. The solution was then heated to 190°F. Clean SAE 1010 cold-rolled steel panels were then treated in the bath for 15 minutes, water rinsed, and dried via compressed air. The panels had adherent dark gray coatings. Similar results were obtained when aniline, N-ethylaniline and pyridine were substituted for the triethanolamine.

**EXAMPLE 6**

Clean spark plug shells employed in Example 3 were treated in a 1.5 weight % NH₄NO₃ solution containing 9 ppm NO₂⁻ for 15 minutes at 195°F. Following water rinsing, the shells were dipped in a water-emulsified rust preventive oil for 3 minutes at room temperature. The black color of the resultant coating was comparable in every way to those treated in a conventional alkaline bath.

**EXAMPLE 7**

Several previously weighed SAE 1010 cold-rolled steel panels were cleaned in a conventional alkaline immersion cleaner and were treated in a 0.75% ammonium nitrate solution for fifteen minutes at 205°F to give a black oxide coating. After water rinsing, the panels were air-dried and reweighed, and it was found that they had lost an average of 664 mg. per ft². The panels were then stripped along with a clean but uncoated panel in an inhibited hydrochloric acid solution and found to have an average coating weight of 283 mg per ft². Thus, a maximum of 30% of the reacting metal finds its way into the black oxide coating.

**EXAMPLE 8**

Spark plug shells composed of SAE 1106 and SAE 12L14 alloys were contacted with a bath containing 108 g/l NaNO₃, 4 g/l NH₄NO₃ (mole ratio NH₄:NO₃ = 0.038:1) at a pH of about 5.5 - 6.0 and a temperature of 200°-210°F for 15-18 minutes. Glossy black adherent coatings were obtained on both types of alloys. Similar results for both were obtained at mole ratios of NH₄NO₃ of from 0.15 to 0.13. As neutral nitrate salts, comparable results were obtained by substituting calcium, magnesium and potassium salts. Excellent results were obtained when the cationic nitrogen was derived from triethanolamine, pyridine, aniline, N-ethylaniline and urea. Total nitrate concentration varied from 87 g/l or 24 g/l.

What is claimed is:

1. A method of forming a corrosion resistant and decorative black coating on a predominately iron surface of a workpiece, comprising contacting said surface with an aqueous acidic solution consisting essentially of:
   1. at least 0.01 wt. % nitrate ion and
   2. a soluble nitrogen containing cation selected from the group consisting of
      a. ammonium derivatives of which have the formula

![Chemical Structure](image)

and,

b. pyridinium derivatives which have the formula

![Chemical Structure](image)

wherein R₁ through R₈ are independently selected from hydrogen alkyl, aryl, and aryl radicals containing —OH, >C=O, or —NH₂ substituents and wherein the nitrogen containing ion is present in a mole ratio of cationic nitrogen to nitrate of from 0.001 to 10:1 at a temperature of from 140°F up to the boiling point of the solution.

2. The method of claim 1 wherein the pH of said solution is between about 4.0 and 6.8.

3. The method of claim 1 wherein said solution additionally includes an oxidizing agent as an accelerating compound.

4. The method of claim 3 wherein said oxidizing agent is the nitrite ion and is present in an amount between 0.0005 and 0.01 weight %.

5. The method of claim 1 wherein said bath is substantially free of dissolved phosphates.

6. The method of claim 1 comprising the additional subsequent step of contacting said workpiece with a rust preventive oil.

7. The method of claim 1 wherein said nitrogen cation is ammonium.

8. A method of preparing a bath as defined in claim 1 wherein 5 - 50 ppm nitrite ion is added prior to introducing said workpiece.

9. The method of claim 1 wherein said solution includes at least one surfactant to improve the solubility of the remaining components.

10. The method of claim 1 wherein the temperature of the solution is maintained at at least 160°F.