METHOD AND COMPOSITION FOR BLACKENING METAL ARTICLES


No Drawing. Filed Jan. 23, 1959, Ser. No. 788,511

10 Claims. (Cl. 148—6.24)

The invention relates to an improved method and chemical composition for the production of black coatings on metals.

Hereinafter, in providing black coatings on ferrous metals by means of baths of the conventional blackening compositions, contaminations thereof by red iron oxide, copper or zinc as occur in the use of the bath produced a red smut on the blackened surface. Efforts to overcome this have been made by adding to the composition small quantities of sodium sulphide. This was effective to some degree. However, it reacted quickly with the contaminant and was soon used up so that it had to be replaced frequently.

The present invention overcomes this and other difficulties with the prior baths by providing a novel method and composition for producing black oxide coatings on ferrous and other metals which is effective in preventing smut, which provides improved reactivity of the blackened articles, reduces dragout, and improves the penetrability of the composition into small crevices to ensure a more uniform surface blackening.

In carrying out the invention I have found that if any one of a cyclic sulphur-containing organic compound chosen from the group consisting of 2-mercaptobenzothiazole, benzothiazyl disulphide and 2-mercaptoimidazolone is added even in small quantities to a conventional bath the tendency to deposit the usual smut is quickly eliminated and the effectiveness of the material in the bath lasts over a longer period of time than heretofore accomplished.

When it is desired to improve the reactivity of the coated articles and to reduce the dragout, I have found that the conventional blackening solution can be modified by putting into it a small percentage of alkyl naphthaleine sulfonate. In cases where greater penetrability of the solution is desired, as in blackening a plurality of small articles, such as paper clips and the like, the penetrability of the compound into the crevices between the articles can be increased to instore a more uniform blackening thereof by adding to the composition small amounts of a sulfonated dye chosen from the group consisting of di-phenyl—dis-azo-bis-8-anilino-1-naphthol-3,6 disulfonic acid, 8-anilino-5-(p-hydroxy anilino)-1-naphthalene sulfonic acid and anthraquinone vat dyes. Preferably the metallic salts thereof (particularly sodium salts) are used in the composition.

Conventional blackening baths are made up of a blackening salt composition consisting essentially from 50—90 parts by weight of an alkali metal hydroxide and from 0.1—50 parts by weight of an alkali metal nitrate and/or from 0.1—50 parts by weight of an alkali metal nitrite. The alkaline metals can be potassium or sodium. The composition is mixed with water so as to produce a bath solution having a boiling temperature of between 225° and 325° F. when sufficient heat is applied thereto. The terms “conventional blackening composition” or “conventional blackening bath” as used herein shall designate such composition or bath.

In order to prevent the conventional blackening bath, when contaminated with red iron oxide, copper or zinc, from producing a reddish smut on the blackened ferrous metal articles, I add to the bath a small amount, i.e., in the range of between a trace to 20 parts by weight, and preferably .25 part by weight, of any one of a cyclic sulphur-containing organic compound chosen from the group consisting of 2-mercaptopbenzothiazole, benzothiazyl disulphide and 2-mercaptoimidazolone. Articles blackened in this bath showed no signs of smut and had a clear black surface. Furthermore, there was no substantial foaming of the bath at the operating temperature of the bath which was approximately 290° F. and the bath will retain its properties of preventing the smut for a long period of time.

For example, a sample was taken from a production run of a conventional blackening bath. It showed a contamination of 1.07 parts by weight of colloidal red iron oxide. The sample of the bath was heated to a boiling temperature of 290° F. and steel panels were immersed in the bath for fifteen minutes, after which they were rinsed and dried and a red smut of colloidal iron oxide was on the pieces. Thereafter .0325 part by weight of 2-mercaptoimidazolone was added to the sample of the bath and steel plates were immersed in the bath for the same time and removed. They had a good black finish without any deposit of red smut. Similar results were obtained with solutions contaminated with copper braze materials and zinc and the addition of 2-mercaptoimidazolone cleared up the red smut condition resulting in a good black finish. Tests using 2-mercaptopbenzothiazole and benzothiazyl disulfide in place of the 2-mercaptoimidazolone were made and these too prevented red smuts from being deposited on the plates.

In accordance with the present invention the reactivity and dragout characteristics of the conventional blackening composition have been improved by the addition thereof of small amounts of low chloride content alkyl naphthalene sodium sulfonate. One such material is sold under the trade name Petro AA by Petrochemical Co., Long Beach, California. This material, in the range of 0.01—15 parts by weight, is added to the conventional blackening composition and it is found that the articles when immersed in the bath formed by said composition and removed therefrom are more readily rimed of the blackening bath.

For example, two baths were made up from a conventional blackening composition comprising 70 parts by weight of sodium hydroxide, 10 parts by weight of sodium nitrite and 20 parts by weight of sodium nitrite. The compositions were mixed with sufficient water to attain a boiling temperature between 255—320° F. In this particular example, a boiling temperature of 290° F. was used. To one bath .025 part by weight of an alkyl naphthalene sodium sulfonate was added. Steel panels were immersed in each of the solutions and boiled at 290° F. for five minutes. They were removed from the solutions and the plates coming from the bath having additional material therein were observed to have the solution of the bath running off readily therefrom while the plates from the conventional bath had droplets of bath solution
clinging to the panel without dropping off. When both were rinsed, it was observed that the first samples were readily rinsed clean and the material thereon while it was more difficult to remove the conventional bath material from the second samples.

A further test was made to determine the amount of dragout from the baths. In this, a panel from each bath was allowed to drain for thirty seconds and then was placed in separate beakers containing 200 milliliters of distilled water and stirred thoroughly. The rinse water in the beakers was then titrated. It was found that 43.2 milliliters of N/10 acid was used to titrate the water in the beaker having the plate from the standard blackening solution whereas only 35 milliliters of the acid was required to titrate the water in the beaker having the plate from the solution of the present invention showing that there was 19% less dragout resulting from the use of the present solution than from the conventional solution.

This test also shows that less bath material remained on the plate of the present invention which also made it easier to rinse to provide clean surfaces thereon.

In some cases it has been found that the conventional blackening bath will not penetrate into crevices and around small articles to produce a uniform black finish thereon, such as, for example, a basket of paper clips or the parts immersed in the bath. In accordance with the present invention it has been discovered that the penetrability of the blackening bath can be improved by adding thereto between .0001 to 20 parts by weight of a metallic salt (preferably sodium) of a sulfonated dye chosen from the group consisting of di-phenyl-dis-azo-bis-8-amino-1-naphthol-3,6 disulfonic acid, 8-anilino-5-(p-hydroxy anilino)-1-naphthalene sulfonic acid and the sulfonated anthraquinone vat dyes. For example, to a conventional blackening solution comprising 82 parts by weight of sodium hydroxide, 13 parts by weight of sodium nitrite and 5 parts by weight of sodium nitrate was added .005 part by weight of sodium salt of di-phenyl-dis-azo-bis-8-amino-1-naphthol-3,6 disulfonic acid.

A bath was made by mixing this composition with sufficient water to attain a boiling temperature of between 255-320°F. A basket full of small articles packed therein was inserted in the bath and the bath maintained at a temperature of about 290°F. for a predetermined time to complete the blackening operation after which the articles were removed. They were uniformly blackened throughout the surface thereof showing that the bath penetrated into the crevices and crevices and the articles to produce the required blackening thereon.

Similar tests were made using the 8-anilino-5-(p-hydroxy anilino)-1-naphthalene sulfonic acid and anthraquinone vat dyes and in each case the penetrability of the solution was improved.

From the foregoing it will be seen that the conventional blackening composition is improved in three aspects—namely, to eliminate smut from the articles, to improve the rinsability and reduce dragout from the solution and to increase the penetrability of the solution. It is within the purview of the present invention that conventional blackening solutions and the method of blackening foreign articles therewith can be improved in each of the three respects separately or any combination thereof as may be required. For example, in order to secure the maximum efficiency from the conventional blackening composition there was added thereto .05 part by weight of 2-mercaptobenzothiazole, .075 part by weight of alkyl naphthalene sulfonate and .005 part by weight of sodium salt of di-phenyl-dis-azo-bis-8-anino-1-naphthol-3,6 disulfonic acid. This composition was made into a bath by the addition of sufficient water to attain a boiling temperature of 255-325°F. The ferrous metal pieces were inserted in the bath for the requisite time and the resulting pieces had a clean black surface which was free of smut, was readily rinsed and in which the coloring composition penetrated into all small crevices so as to provide a uniform black coating on the articles.

Variations and modifications may be within the scope of the claims and portions of the improvements may be used without others.

I claim:

1. A composition for the surface blackening of metal articles consisting of a mixture of conventional blackening composition containing from 50.2 to 190 parts by weight of blackening salts and having added thereto from 1 trace to 20 parts by weight based upon the weight of the conventional blackening composition of at least one cyclic sulphur-containing organic compound chosen from the group consisting of 2-mercapto-benzothiazole, benzothiazyl disulphide and 2-mercaptopimidine, wherein the cyclic sulphur-containing organic compound is added thereto at a rate above 0.05 parts by weight.

2. The composition of claim 1 wherein there is added .0001 to 20 parts by weight based upon the weight of the conventional blackening composition of an alkyl naphthalene sodium sulfonate whereby the rinsability of the article is improved and the dragout from the bath is decreased.

3. The composition of claim 1 wherein there is added .0001 to 20 parts by weight based upon the weight of the conventional blackening composition of a metallic salt of a sulfonated dye chosen from the group consisting of di-phenyl-dis-azo-bis-8-amino-1-naphthol-3,6 disulfonic acid, 8-anilino-5-(p-hydroxy anilino)-1-naphthalene sulfonic acid and anthraquinone vat dyes whereby said composition is provided with improved penetrability into small crevices.

4. The composition of claim 3 wherein there is added .0001 to 20 parts by weight based upon the weight of the conventional blackening composition of an alkyl naphthalene sodium sulfonate whereby the rinsability of the article is improved and the dragout from the bath is decreased.

5. A method for the surface blackening of metal articles consisting essentially of a conventional blackening composition containing from 50.2 to 190 parts by weight of blackening salts and having added thereto .0001 to 20 parts by weight based upon the weight of the conventional blackening composition of an alkyl naphthalene sodium sulfonate whereby the rinsability of the article is improved and the dragout from the bath is decreased.

6. The composition of claim 5 wherein there is added .0001 to 20 parts by weight based upon the weight of the conventional blackening composition of a metallic salt of a sulfonated dye chosen from the group consisting of di-phenyl-dis-azo-bis-8-amino-1-naphthol-3,6 disulfonic acid, 8-anilino-5-(p-hydroxy anilino)-1-naphthalene sulfonic acid and anthraquinone vat dyes whereby said composition is provided with improved penetrability into small crevices.

7. The process of blackening metal articles which comprises the steps of preparing a bath consisting essentially of a conventional blackening composition containing from 50.2 to 190 parts by weight of blackening salts and at least a trace to 20 parts by weight based upon the weight of the conventional blackening composition of at least one cyclic sulphur-containing organic compound chosen from the group consisting of 2-mercapto-benzothiazole, benzothiazyl disulphide and 2-mercaptopimidine, said bath being prepared by adding the mixture to water in sufficient amounts to bring the boiling temperature of the solution to a point between 255-325°F., immersing the articles in the solution while maintaining the boiling temperature of the bath for a period of time sufficient to impart the desired smut free black coating to the articles, removing the articles from the bath and rinsing the articles to remove the solution remaining thereon.

8. The process of claim 7 in which .005 part by weight based upon the weight of the conventional blackening composition of sodium salt of di-phenyl-dis-azo-bis-8-amino-1-naphthol-3,6 disulfonic acid is added to the composition.

9. The process of claim 7 in which .075 part by weight
based upon the weight of the conventional blackening composition of alkyl naphthalene sodium sulfonate is added to the composition.

10. The process of claim 9 in which .005 part by weight based upon the weight of the conventional blackening composition of sodium salt of a sulfonated dye chosen from the group consisting of di-phenyl-dis-azo-bis-8-amino-1-naphthol-3,6 disulfonic acid, 8-anilino-5-(p-hydroxy anilino)-1-naphthalene sulfonic acid and anthraquinone vat dyes is added to the composition.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,960,420

Abraham J. Mitchell

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 47, for "001" read -- .0001 --;
column 4, line 28, for "dis" read -- dis- --; line 29, for "1" read -- 1--.

Signed and sealed this 25th day of April 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents