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METHOD FOR THE PRODUCTION OF BLACK OXIDE COATINGS ON STEEL AND IRON AND COMPOSITION THEREFOR

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This invention relates to an improved chemical composition for the production of black oxide coatings on steel and iron and in particular relates to materials for blackening steel in the presence of copper.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the processes, steps and combinations pointed out in the appended claims.

The invention consists in the novel steps, processes, compositions and improvements herein shown and described.

It has been possible up to the present time to produce satisfactory oxide coatings on steel in the absence of copper, but deposits of smut and light and dark areas are generally found when copper is present in the blackening solution.

Moreover, when articles assembled by copper brazing or by silver brazing alloys containing copper are to be blackened, copper frequently dissolves in the solution to affect its efficiency and the blackness of the steel parts and in addition the metal used for brazing is not blackened.

The following compositions are typical of the conventional blackening baths which are used at the present time for the successful blackening of steel. These baths will produce a smut on the parts when copper is present in amounts as low as .01 of 1%. Brazed joints containing copper cannot be blackened in any of the following conventional compositions:

	A	B	C	D	E	F	G
Sodium Hydroxide...parts by weight	66	70	75	80	83	90	50
Potassium Nitrate.....do	31	----	----	----	----	----	50
Potassium Nitrite.....do	3	----	----	----	----	----	----
Sodium Nitrate.....do	----	15	15	----	11	----	----
Sodium Nitrite.....do	----	15	10	20	6	10	----

These formulae are used by dissolving in water until the boiling temperature of the water solution has risen to a point between 260 and 320° F. and the steel parts to be blackened immersed therein.

We have found that the addition of a compound chosen from the group consisting of sodium thiocyanate, thiourea, and alkyl thioureas such as diethyl thiourea, and dibutyl thiourea, will prevent the deposition of a copper smut on steel parts and maintain the blackening efficiency of the solution when blackened in accordance with the usual methods in any of the conventional types of oxidizing baths used for this purpose. We have also found that together with the addition of such a compound to the standard oxidizing bath an added small amount of nickel or cobalt will further improve the results of the blackening process. When an additional small amount of nickel or cobalt is used there is, in fact, a brilliant, lustrous uniform deep black coating having a slightly blue tint produced on

the surface of the steel. Spectrographic examination of the black coating showed it to contain nickel when nickel is used in the bath and cobalt when cobalt is added to the bath. Not only is the efficiency of the bath maintained in the presence of copper by the use of these materials, but the rate of production of the black coating is increased by the addition of nickel or cobalt so that the time necessary for producing satisfactory black finishes is substantially lowered. In baths where steel components are joined by brazing alloys such as copper or silver, the coatings produced are uniform and highly satisfactory both on steel and brazing alloy. It has been very difficult to produce satisfactory black coatings on cast iron with conventional blackening baths; even those containing sodium thiocyanate, thiourea and substituted thiourea have not given as black a finish as might be desired. With the use of the nickel or cobalt containing baths, it has been possible to produce deep black coatings on cast iron in short periods of time.

Nickel and cobalt appear to be interchangeable in these formulas but nickel, however, is preferred for economical reasons.

The compounds sodium thiocyanate, thiourea, diethyl thiourea and dibutyl thiourea, we have found to be effective in the following order:

(1) Sodium thiocyanate
(2) Diethyl thiourea
(3) Dibutyl thiourea
(4) Thiourea

with sodium thiocyanate being the most effective and thiourea, the least effective.

The thiocyanates and thioureas with or without the addition of nickel or cobalt may be used in amounts up to 25%, but when more than 5% of these compounds are used, a small amount of surface deposit forms which however, can be readily removed, leaving a good black underneath. Where less than 5% of these materials are used, no surface deposit appears to form. While our formulae show the use of sodium thiocyanate, we do not limit ourselves to the use of the sodium salt. Other soluble thiocyanates such as potassium and lithium may be used.

Likewise, we do not limit ourselves to the thioureas mentioned as it may be readily seen that other substituted thioureas such as diamyl and dihexyl may be useful for this purpose. The use of these materials in addition to preventing copper from producing smuts or mottled finishes, on the steel also prevents the copper from affecting the efficiency and life of the bath. These compounds appear to maintain the original blackening efficiency of the bath as long as the compound used is maintained in accordance with the amounts prescribed above. Parts blackened in these baths have at least as good corrosion resistance as those blackened in the conventional blackening baths and in some instances superior corrosion resistance has been noted. While the customary blackening baths do not produce a black coating on copper and silver alloys used for joining metal, our compositions do produce a black finish on such alloys, particularly those used in the joining of ferrous metals so that a more or less uniform black finish is produced in spite of the use of dissimilar metals.

When using nickel or cobalt we have also found that the amount of nickel required is not critical as long as at least .1% is present. We have used as high as 25% nickel in the bath with no detrimental results, but this is not believed to be economical, and we have found that 1% of nickel gives satisfactory results.

EXAMPLES

The following examples will illustrate the scope of our invention:

Example 1

	Parts by weight
Sodium hydroxide	66
Potassium nitrate	31
Potassium nitrite	3
Sodium thiocyanate	1

Sufficient amounts of the above are added to water to produce a mixture boiling in the range of 260 to 320° F. and an assembly consisting of polished steel parts held together with a copper brazing alloy is immersed in the bath for a period of 20 minutes. At the end of this time the assembly is removed from the bath, rinsed in running cold water and dried. The whole assembly including the brazed alloy joint was found to be completely blackened with no smut. A duplicate assembly treated in a conventional production blackening bath was not blackened at the brazed joint and showed objectionable smut.

To the above composition of Example 1, .25 part by weight of nickel nitrate was added and the same procedure followed. The black finish had a blue tint and was lustrous, uniform and without smut.

Example 2

	Parts by weight
Sodium hydroxide	70
Sodium nitrate	15
Sodium nitrite	15
Diethyl thiourea	1

Sufficient amounts of the above mixture were added to water to produce a boiling temperature of 290° F. and .03 of 1% of copper sulphate in solution was added to the bath. A steel panel immersed in the bath for 15 minutes became oxidized with a uniform coating more black than blue-black and with no evidence of copper smut. Another bath run at the same time, having no diethyl thiourea, showed a heavy reddish smut consisting partly of copper.

Still another bath run at the same time with the addition of 1 part by weight of cobalt chloride showed a more desirable blue-black coating with greater depth of color than the black coating of the first bath.

Example 3

	Parts by weight
Sodium hydroxide	75
Sodium nitrate	15
Sodium nitrite	10
Dibutyl thiourea	1

Sufficient amounts of the above formula were added to water to produce a mixture boiling at 280° F. .03% of copper sulphate was added to this boiling mixture and a polished steel panel immersed in the bath for 10 minutes. A brilliant, lustrous, uniform black coating was produced on the surface of the steel. There was no evidence of production of smut. A similar bath containing no dibutyl thiourea gave a heavy smut on the steel panel.

Still another bath was run with the addition of 5 parts by weight of nickel sulphate. The resultant black coating was of a deeper character than the first bath and had a slightly blue tint on the surface of the steel.

Example 4

	Parts by weight
Sodium hydroxide	80
Sodium nitrite	20
Potassium thiocyanate	1

Sufficient amounts of this mixture were dissolved in water to produce a solution boiling at 300° F. A steel assembly brazed together by means of a copper bearing silver solder was immersed in the bath for a period of one-half hour. At the end of this time, the assembly was rinsed in water and examined. The surface of both the steel and silver solder was completely coated by a black finish with no smut. A similar bath containing no potassium thiocyanate did not blacken the silver solder.

A similar bath containing the potassium thiocyanate and 1 part by weight of nickel chloride produced a blue-black finish.

Example 5

	Parts by weight
Sodium hydroxide	83
Sodium nitrate	11
Sodium nitrite	6
Sodium thiocyanate	2

Sufficient amounts of this mixture were added to water to give a boiling temperature of 320° F. and a piece of low-carbon steel immersed in the bath for a period of 45 minutes. A good black coating was formed on the steel at this time.

Another bath containing 25 parts by weight of nickel nitrate produced a more desirable black with a blue tint.

Example 6

	Parts by weight
Sodium hydroxide	90
Sodium nitrite	10
Sodium thiocyanate	25

Sufficient amounts of this mixture were added to water to give a boiling temperature of 290° F. A piece of gray cast iron was immersed in this bath for a period of 15 minutes. At the end of this time, the cast iron showed a good black. A similar bath without the thiocyanate did not blacken.

A similar bath containing 1 part by weight of nickel nitrate produced a deeper more satisfactory black finish than that produced with the addition of sodium thiocyanate alone and in 25 to 35 percent less time.

Example 7

	Parts by weight
Sodium hydroxide	83
Sodium nitrate	11
Sodium nitrite	6
Sodium thiocyanate	1

Sufficient amounts of this mixture were added to water to give a boiling temperature of 290° F. A piece of 430 grade stainless steel was immersed in the bath for a period of 15 minutes. At the end of this time, the 430 grade stainless steel showed a good black. A similar bath, but containing no thiocyanate, did not blacken the 430 grade stainless steel.

Here again a similar bath containing 1 part by weight of nickel nitrate as well as thiocyanate produced a deeper more satisfactory black.

Example 8

	Parts by weight
Sodium hydroxide	50
Potassium nitrate	50
Sodium thiocyanate	0.1

Sufficient amounts of this mixture were dissolved in water to give a boiling temperature of 312° F. A piece of 0.3 carbon steel was immersed in the bath for a period of 20 minutes. A good black coating was formed on the steel in this period of time. Another bath of the same composition to which had been added 0.1 part by weight of nickel nitrate produced a more desirable black with a blue tint.

The above examples illustrate the wide range of applicability of our invention as well as illustrate the non-critical nature of the components used so that a wide range in amounts of materials can be used satisfactorily in our process.

In the addition of nickel or cobalt we have found generally superior results. Tests made on articles treated

by our process have shown them to be equal or superior to from the standpoint of corrosion resistance when compared with articles produced from conventional baths. In some cases, the corrosion resistance as determined by the salt spray exposure test has been doubled. The appearance of the finished articles is greatly enhanced by this process since with the added nickel or cobalt the black finish has a blue rather than a red tint. The coatings are lustrous and reflective when produced on polished steel parts and are as corrosion resistant as coatings produced in conventional oxidizing baths.

What is claimed is:

1. A composition for the blackening of ferrous metals consisting essentially of alkali metal hydroxide 50 to 90 parts by weight, alkali metal nitrate 0.1 to 50 parts by weight; alkali metal nitrite 3 to 20 parts by weight; together with 0.1 to 25 parts by weight of at least one compound chosen from the group consisting of soluble alkali metal thiocyanates; thiourea and alkyl thioureas.

2. The composition of claim 1 with the addition of 0.1 to 25 parts by weight of at least one soluble salt of the group of metals consisting of cobalt and nickel.

3. A composition for the blackening of ferrous metals and ferrous metals in the presence of copper and copper bearing alloys, consisting essentially of

	Parts by weight
Sodium hydroxide	70
Sodium nitrate	15
Sodium nitrite	15
Diethyl thiourea	1

4. The composition of claim 3 together with the addition of 1 part by weight of cobalt chloride.

5. A composition for the blackening of ferrous metals and ferrous metals in the presence of copper and copper bearing alloys, consisting essentially of

	Parts by weight
Sodium hydroxide	80
Sodium nitrite	20
Potassium thiocyanate	1

6. The composition of claim 5 together with the addition of 1 part by weight of nickel chloride.

7. A composition for the blackening of steel consisting essentially of

	Parts by weight
Sodium hydroxide	83
Sodium nitrate	11
Sodium nitrite	6
Sodium thiocyanate	1

8. The composition of claim 7 together with the addition of 1 part by weight of nickel nitrate.

9. A bath for the blackening of ferrous metals and ferrous metals in the presence of copper and copper bearing alloys consisting essentially in aqueous solution of alkali metal hydroxide, 50 to 90 parts; alkali metal nitrite, 0.1 to 50 parts; alkali metal nitrate, 3 to 20 parts; and at least one compound chosen from the group consisting of soluble alkali metal thiocyanates, thiourea, and alkyl thioureas, 0.1 to 25 parts; all parts by weight.

10. A bath as in claim 9 together with the addition of .1 to 25 parts by weight of at least one soluble salt of the group of metals consisting of cobalt and nickel.

11. The process of blackening ferrous metal articles which comprises the steps of preparing a bath having a composition consisting essentially within the following limits of alkali metal hydroxide, 50 to 90 parts; alkali metal nitrite, 0.1 to 50 parts; alkali metal nitrate, 3 to 20 parts; and at least one compound chosen from the group consisting of soluble alkali metal thiocyanates, thiourea, and alkyl thioureas, 0.1 to 25 parts; all parts by weight; 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 260° F. and 320° F., and immersing the articles in the solution while maintaining the boiling temperature of said bath for a period of time sufficient to impart the desired black coating to the articles.

12. The process of claim 11 in which 0.1 to 25 parts by weight of at least one soluble salt of the group of metals consisting of cobalt and nickel is added to said composition.

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