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COMPOSITION AND METHOD FOR BLACKENING METAL ARTICLES

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ABSTRACT OF THE DISCLOSURE

A composition for producing black oxide coatings on ferrous metals comprising a liquid mixture of sodium hydroxide, sodium nitrate, sodium nitrite, and water is improved by the addition of triethanolamine or other iron sequestrants.

This invention relates to improved chemical compositions and their use for production of black oxide coatings on ferrous metals.

It is already known that protective black oxide coatings are produced on ferrous metal articles when such articles are immersed in strongly alkaline solutions or salt baths based on alkali metal salts including the nitrates, nitrites and hydroxides. One group of such baths is described in U.S. Pat. Nos. 3,085,035 and 2,960,420, the disclosures of which are incorporated by reference as illustrative of the prior art.

In order to perform satisfactorily these and similar prior art baths must be maintained at relatively high temperatures which may be sufficient adversely to affect the properties of heat treated articles. They must be held within a much narrower temperature range of operation than the compositions of the present invention, and are often limited in the alloys which they will blacken. Prior art baths, furthermore, tolerate only small amounts of iron before giving red deposits on surfaces of treated articles, and are less desirable economically because of greater chemical consumption.

A principal object of this invention is to provide compositions which give oxide coatings superior in depth of color and corrosion resistance.

Another object of the invention is to provide blackening compositions which can be stored in either dry or liquid form, the latter form obviating the mixing of highly alkaline powder with water, and the attendant risk of boil-over or danger.

A further object of the invention is to provide blackening compositions as liquid baths having a greatly extended service life as compared to prior art baths.

Still another object of the invention is to provide blackening compositions which are operable and produce good results over a much wider temperature range and with which blackening times are relatively shorter than with prior art baths.

A still further object of the invention is to provide blackening compositions which are useful in baths operable at lower temperatures than are prior art baths, in the range, for example, of 245° F. to 290° F., or 20° F. to 60° F. lower than operable temperature ranges for prior art baths.

These and other objects are achieved by compositions consisting essentially of sodium hydroxide, sodium nitrate, and sodium nitrite, to which triethanolamine or other specified additives have been added, which compositions may be stored as dry mixtures or as solutions made up with water.

Incorporation of an iron sequestrant or combination of iron sequestrants into a strongly alkaline bath containing sodium nitrate and sodium nitrite results in a

superior black oxide coating on ferrous metal. It is important that a sequestrant which specifically sequesters iron in highly alkaline mediums be used in the present invention. It has been found that sequestrants which sequester iron in highly alkaline mediums at bath temperatures above 245° F. in accordance wth the principle of this invention are certain alcohol amines, sorbitol and its derivatives, certain metal gluconates and derivatives thereof, certain metal nitriloacetates and derivatives thereof, and combinations of the foregoing. Examples of iron sequestrants suitable in the present invention are triethanolamine, sodium gluconate, sodium heptagluconate, sorbitol, diethanolamine, monoethanolamine, sodium nitriloacetate, etc. Of these, triethanolamine is superior and the preferred sequestrant because of bath stability, lack of foaming, and superior sequestration of iron. Cations other than sodium are equally effective; and bath alkalinity can be achieved with sodium or potassium hydroxides. Superiority of the black oxide coating which results is in both appearance and corrosion resistance. Superiority lies also in lower temperature operations and in greater diversity of iron alloys that can be processed successfully.

Use of the compositions of the present invention in liquid form is an advance over the prior art because of the advantages of a composition approximating that of a working bath so that additions can be made at optimum bath temperature without risk of boil-over or danger. The latter consideration is important because of the fact that the bath is operated at high temperatures.

Although in the examples which follow, the sodium salts are specified as preferred, it is also possible to use the potassium or lithium salts in their stead.

The broad ranges of the three salt constituents, based on the weight of the actual blackening bath, i.e. with the water and iron sequestrant included, is as follows:

	Percent by weight
Sodium hydroxide	32–55
Sodium nitrate	1–8
Sodium nitrite	0.5–6

The above composition when made up to 100% by the addition of water acts as a blackening bath for many ferrous metals, but we have found that its effectiveness can be greatly extended by the addition of an iron sequestrant, notably triethanolamine. Although triethanolamine is the preferred sequestrant in the composition of this invention, the following iron sequestering agents may also be used:

diethanolamine
monoethanolamine
sodium gluconate
sodium heptagluconate
sodium nitriloacetate
sorbitol.

Up to 10% of iron sequestrant additive may be used, alone or in mixtures of two or more. With triethanolamine, sodium gluconate, or sodium heptagluconate, a concentration of 0.05 to 2% suffices. For the other iron sequestrant additives, the concentration should range between 1 and 10%.

When iron sequestrants such as those indicated hereinabove are added to the alkaline blackening baths of this invention, the following advantages are gained over prior art baths:

(1) more intense black color,
(2) coatings of increased corrosion resistance,
(3) lower operating temperature ranges,
(4) ease and safety in charging and making additions to tanks,
(5) ability to coat alloys of a wider range,
(6) wider operating temperature ranges.

In Table I, below, exemplary bath compositions are set forth.

TABLE I

Bath No.	1	2	3	4	5	6	7	8	9	10
Component in weight:										
NaOH	32	36	36	36	36	36	36	38	46	55
$NaNO_2$	6	8	8	4.5	4.5	4.5	4.5	7	1	4
$NaNO_3$	4	2.5	6	2.5	2.5	2.5	2.5	0.5	0.4	2
Additive*	1	0.7	0.7	2.0	0.05	10	1.0	0.7	0.7	0.5
Water	57	52.8	49.3	55	56.95	47	56	53.8	51.9	38.5

*Additives:
Baths 1, 2, 3, 8, 9, 10: Triethanolamine.
Baths 4, 5: Total of triethanolamine, sorbitol, sodium gluconate or sodium heptagluconate (alone or mixtures).
Baths 6, 7: Total of diethanolamine, monoethanolamine and sodium nitriloacetate (alone or as mixtures).

The common characteristic of the additives in the above baths is that each of the additives complexes or sequesters or chelates iron in highly alkaline solution.

Preferred compositions of the present invention boil at temperatures between about 245° F. and 290° F. and comprise by weight:

	Percent
Sodium hydroxide	34–38
Sodium nitrite	4.5–6.0
Sodium nitrate	2.2–4.0

with from 0.05 to 2% of triethanolamine additive and with water to make 100%.

Compositions defined immediately above using triethanolamine as the sequestrant represents preferred embodiments of the invention.

To practice the invention, a mixture of the dry ingredients (sodium hydroxide, sodium nitrite, and sodium nitrate) is formed, and can then be stored as a separate product, or may be made up with the required amount of water to achieve the desired bath concentration. The triethanolamine or other sequestrant is added up to the limit of its solubility and then may be added in increments as the bath is used.

As indicated hereinabove the preparation and storing of these compositions in liquid form represents a distinct advantage, sparing the user's having to dissolve strong alkali in high concentration. Using liquid forms of the compositions of the invention, thus, the user need merely pump the liquid into the tank and heat to boiling before immersing articles to be blackened.

In tests with operating blackening baths, improvement in the quality of the black is noticeable upon addition of 0.09% triethanolamine. A very pronounced beneficial effect was observed with the addition of 0.5% triethanolamine, but when 2% of triethanolamine was used a smut developed which was easily removed by a subsequent standard cleaning operation.

Spent baths based on the prior art which have become contaminated with iron and which thus have reached the end of their operating life usually turn brownish red and such baths have been brought back to operating condition with elimination of the brownish red color by addition of triethanolamine or other of the specified iron sequestrants.

The blackening bath is used in the usual way, that is to say, once the components have been brought together, the bath is heated to almost the boiling point and then the articles to be blackened are immersed in the heated composition and are held therein until the desired depth of blackening has been achieved. On removal from the bath the articles are permitted to dry in air and subsequently rinsed to remove any salt residue.

Having now described the invention, it is not intended that it be limited, except as may be required by the appended claims.

What is claimed as new is as follows:

1. A blackening composition for ferrous articles consisting essentially of the following in percent by weight:

	Percent
Alkali metal hydroxide	32–55
Alkali metal nitrite	1–8
Alkali metal nitrate	0.5–6
Iron sequestrant	0.05–10

balance to make 100%, water; said iron sequestrant being stable in highly alkaline solutions at temperatures above 245° F. and capable of sequestering iron introduced into said solution and being selected from the group consisting of alcohol amines, sorbitol and derivatives, metal gluconates and derivatives, metal nitriloacetates and derivatives and combinations thereof.

2. The composition of claim 1 in which the sequestrant is selected from the group consisting of:

triethanolamine
sodium gluconate
sorbitol
monoethanolamine
diethanolamine
sodium nitriloacetate
sodium heptagluconate
and combinations thereof.

3. The composition of claim 1 wherein the alkali metal salts are sodium salts.

4. The composition of claim 3 wherein the proportions are

	Percent
Sodium hydroxide	34–38
Sodium nitrite	4.5–6
Sodium nitrate	2.2–4.0
Iron sequestrant	1–10

5. The composition of claim 1 wherein the iron sequestrant is a member of the group consisting of sodium gluconate, sodium heptagluconate, and triethanolamine; and its proportion is 0.05–2%.

6. A method of extending the useful life of a blackening bath which has lost its ability to blacken ferrous metal objects and which consisted essentially of sodium hydroxide, sodium nitrite and sodium nitrate dissolved in water, which comprises adding up to 10% by weight of an iron sequestrant selected from the group consisting of sodium gluconate, sorbitol, monoethanolamine, diethanolamine, sodium nitriloacetate, sodium heptagluconate, and triethanolamine to said bath.

7. A method of extending the useful life of a blackening bath which has lost its ability to blacken ferrous metal objects and which consisted essentially of sodium hydroxide, sodium nitrite and sodium nitrate dissolved in water, which comprises adding up to 10% by weight of an iron sequestrant selected from the group consisting of sodium gluconate, sodium heptagluconate, and triethanolamine.

8. A blackening composition for ferrous articles consisting essentially of the following in parts by weight:

Alkali metal hydroxide	32–55
Alkali metal nitrite	1–8
Alkali metal nitrate	0.5–6
Iron sequestrant	0.05–10

said iron sequestrant selected from the group consisting of triethanolamine, sodium gluconate, sorbitol, monoethanolamine, diethanolamine, sodium nitriloacetate, sodium heptagluconate, and combinations thereof.

9. The composition of claim 1 in which the percentage by weight of iron sequestrant is 0.05–0.35% and the iron sequestrant is selected from the group consisting of sodium gluconate, sodium heptagluconate, triethanolamine and combinations thereof.

10. The composition of claim 1 in which the percentage by weight of iron sequestrant is 0.35–0.70% and the iron sequestrant is selected from a group consisting of sodium gluconate, sodium heptagluconate, triethanolamine and combinations thereof.

11. The composition of claim 1 in which the percentage by weight of the iron sequestrant is 0.70–10.0% and the iron sequestrant is selected from the group consisting of triethanolamine, sodium gluconate, sorbitol, monoethanolamine, diethanolamine, sodium nitriloacetate, sodium heptagluconate and combinations thereof.

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