This invention relates to methods and compositions for coating iron and steel articles, and has for its main object to correct the poisoning or exhaustion of the bath, and for other objects to avoid a large number of the following disadvantages which have rendered prior expedients along this line unsatisfactory.

The prior coatings have been defective in durability or appearance, being non-adherent or subject to chipping, cracking, crazing, scaling, peeling or powdering off or unable to withstand stamping, rolling or shaping operations, or non-rust resisting, or the coating has been dull or lacking beauty and depth, or not permanent or subject to discoloring with time.

The prior processes have been expensive in the cost to cover or color a unit area, requiring costly equipment or electric set up and power, or difficult or complicated, requiring more than one operation to complete the work, such as spraying, baking, plating or hand sponging, or requiring expert and skilled labor, or being incapable of coloring large quantities in baskets, or yielding non-uniform results or altering dimensions or affecting hardness and elasticity of articles particularly special steels being treated.

The baths employed heretofore have required expensive chemicals or high temperatures or molten salts, or inflammable materials, or have been difficult to prepare or may decompose on standing idle or have short life in operation, or leave a scum or tacky or greasy surface on the article, or attack the surface such as by etching the polish, or deposit oxides of metals electronegative to iron thus decreasing rust resistance, or generate excessive carbonaceous material which interferes with operation, or the baths will not work on common grades of iron or steel.

According to the present invention the bath employed consists of an aqueous solution of an alkali, an oxidizing agent, and an activating agent. The activating agent need not be present in order to operate the bath satisfactorily at first, but it is used as an addition agent for activating the bath and permitting continuous operation of the method.

The alkali used may be for example sodium hydroxide, potassium hydroxide, lithium hydroxide, or in the form of alkali salts such as sodium carbonate or bicarbonate, sodium borate, sodium phosphate, or any combination of these or other alkali forming substance known for this purpose.

The oxidizing agent may be for example a persulphate, peroxide, permanganate, perchlorate, chlorate, nitrate, nitrite, nitrophenol, perborate, of an alkali metal such as sodium, potassium or lithium, or of an alkali earth metal such as barium, or other known oxidizing agent or combination of these, or a material which will form an oxidizing radical in solution in the bath. Lignite may also be used, because our activating agent prevents the lead coating heretofore attendant upon the use of lignite in the bath.

The activating agent may be for example a cyanide, cyanate, sulfite, bisulfite, hyposulfite, thiosulfate, polythionate, oxalate, tartrate, lactate, formate or tannate, of the alkali metals such as sodium, potassium, or lithium, or other suitable reducing agent or combination of these, which will form a reducing or activating radical in solution in the bath.

The following is an example indicating the composition of our bath:

Alkali .............. 1 to 5 lbs., preferably 3 lbs.

Oxidizing agent ....... ½ to 5 lbs., preferably 1 lb.

Water ............... 4 lbs.

In operation this bath is kept at a temperature of from 120° to 155° C. The iron or steel articles such as small indoor hardware are immersed in the bath for a period of ½ minute to 30 minutes depending on the depth of coating desired and the character of the iron or steel being treated. The specific gravity must not be permitted to drop too sharply by dilution with water, nor rise too sharply by evaporation losses. The specific gravity of the bath must be kept within the range of 1.30 to 1.60 measured at 120° C.

After coating a definite amount of metal it is necessary to add a small amount of activating salts or reducing agent, for example, about 0.2% addition by weight of the bath, to enable the bath to continue to function satisfactorily for the coating. This addition permits a further definite amount of metal to be coated, when a subsequent further addition of activating salts must be added. This process can be continued practically indefinitely, thus permitting continuous operation of the bath. There are definite limits to the amount of activating salts which can be added to the bath in order for the same to function properly.

It has also been observed that a fresh bath will function satisfactorily at the lower temperatures of the operating range given whereas an older bath requires somewhat higher temperatures.

Certain steels and iron require a preliminary treatment to activate their surfaces before entering them in the bath. This treatment used for cast iron, stainless steel, and other ferrous metals
which ordinarily react differently to our bath consists of immersion in a 5 to 10% solution of hydrofluoric acid for one to thirty minutes and rinsing off in water.

The composition of the bath can be varied considerably. For example an ounce or two of sodium nitrite could be used instead of the preferred pound per gallon of water.

The nitrite baths are poisoned by the presence of iron which prevents them from functioning as a coating, blackening or coloring agent for steel or iron.

We have discovered that this deleterious influence can be overcome by the addition of sodium cyanide, which converts the positive charged iron into negative charged radical which no longer interferes with the working of the bath. However, the amount of sodium cyanide is definite and must not be in excess because then the bath merely etches the steel instead of coating or blackening it. In other words, the amount of sodium cyanide added must be just sufficient to react with the iron that goes into the solution during the coating or blackening process.

The operation of the bath can be controlled by actual analysis and by keeping the ratio between the cyanide additions and the area of the work put through within definite limits.

As a specific example of our process we start with a fresh bath of the following composition: Sodium hydroxide 3 lbs. Sodium cyanide 1 lb. Water 4 lbs.

Operating temperature range 120 to 150° C. Optimum 135 to 145° C. Time five seconds to thirty minutes depending on the degree of coating or shade of coloring desired.

One gallon of this bath will treat approximately thirty square feet of steel before it will be necessary to add activating salts. This point of temporary exhaustion is always indicated by a lack of depth of the coating or usual color, or none at all.

Sodium cyanide is added just before the bath begins to lose its coating or coloring power, in amount of from 0.1 to 5.0 pounds per 100 pounds of bath. Optimum ½ lb.

If desired the activating salts may contain in addition to sodium cyanide some caustic soda and sodium nitrite to aid in replacing losses due to drain-out of the coloring solution by the steel.

During operation of the bath, control of the same may be obtained by one of several methods, as follows:

1. Chemical analysis for cyanide, nitrite, and caustic soda.

2. Observation of depth of color or coating on a test piece of steel immersed for a standard time of a few seconds and comparison thereof with standard test pieces previously treated in a fresh bath.

3. Control bath to give continually uniform results by utilization of the definitely established data and facts relating to ratio of surface steel which can be colored to a unit of fresh bath, and to the ratio of area of steel which can be colored by addition of a unit amount of activating salts (sodium cyanide) to the bath.

Once the bath is in operation the process can be continued indefinitely, as the weakened bath can be repeatedly regenerated.

The ratio of the amount of steel the bath will color, from the time of addition of the activating salts, NaCN, to the next successive addition per unit amount of NaCN is 100 sq. ft. ¼ lb. NaCN

The bath if operated without use of activating salts soon becomes poisoned apparently by accumulation of excess of iron in the form of positively charged ions. The bath soon fails to coat or color.

By the addition of activating salts such as NaCN the excess iron ions are removed by a chemical reaction with the NaCN, forming NaFe(CN)₅, thus changing the iron from a positively charged radical to a negatively charged radical.

This reaction is undoubtedly the same as the well known chemical reactions showing the formation of ferrocyanide from Fe(OH)₃ and NaCN, as follows:

Fe(OH)₃ + 2 NaCN = 2 NaOH + Fe(CN)₅

We claim:

1. Method of surface treating ferrous metal articles, which comprises immersing said articles in an aqueous solution of an alkali and an oxidizing agent, and regenerating said bath by adding an activating agent differing in chemical composition from either of the two aforementioned substances, and capable of forming complex ions with ions of iron resulting from previous operation and prevent them from inhibiting the further operation of the unspent bath.

2. Method of surface treating ferrous metal articles, which comprises progressively immersing said articles in an aqueous solution of an alkali and an oxidizing agent whereby chemical action takes place at the surface of said articles but said solution becomes inefficient due to inhibiting effect of iron ions accumulating from said action, and at least partly restoring the efficiency of said solution by adding an activating agent other than said oxidizing agent which eliminates the inhibiting effect of said iron ions by chemically converting them into substances harmless to the coloring powers of the bath.

3. Method of coating iron or steel articles, which comprises immersing said articles in an aqueous solution of an alkali and an oxidizing agent whereby chemical action takes place at the surface of said articles but said solution becomes inefficient due to inhibiting effect of iron ions accumulating from said action, and at least partly restoring the efficiency of said solution by adding an activating agent other than said oxidizing agent which eliminates the inhibiting effect of said iron ions by chemically converting them into substances harmless to the coloring powers of the bath.

4. Method of surface treating ferrous metal articles, which comprises progressively immersing said articles in an aqueous solution of an alkali and an oxidizing agent, and regenerating said bath by the addition of ½ pound per 100 square feet of article surface coated of an activating salt which changes the positively charged iron resulting from previous operation into a negative charged radical.

5. Method of surface treating ferrous metal articles, which comprises progressively immersing said articles for a period of from ¼ to 30 minutes in an aqueous solution of an alkali and an oxidizing agent while maintaining said solution at a temperature of between 120° and 155° C., and regenerating said bath by the addition of an activating salt which changes the positively charged iron resulting from previous operation into a negative charged radical.
6. Method of coating iron or steel articles which comprises immersing said articles in a bath of an aqueous solution of weight 2 to 5 parts alkali and 1/2 to 5 parts oxidizing agent to 4 parts water, and successively coating other articles in said bath while maintaining the bath at a temperature between 120°C and 155°C, and regenerating said bath by the addition of 1/2 pound of activating salt which reacts with the iron ions resulting from previous operation and forms therewith complex ions which prevent them from inhibiting the operation of the unspent bath per 100 square feet of article surface coated.

7. Method of coating iron or steel articles which comprises immersing said articles in an aqueous solution of weight 2 to 5 parts alkali and 1/2 to 5 parts oxidizing agent to 4 parts water, and regenerating said bath by adding 0.1 to 5.0 pounds for 100 pounds weight of the bath of a regenerating agent which reacts with iron ions resulting from previous operation to counteract any inhibition thereby of the unspent bath.

8. Method of coating iron or steel articles which comprises immersing said articles for a period of from 1/4 to 30 minutes in a bath of an aqueous solution consisting of weight 2 to 6 parts alkali and 1/2 to 5 parts oxidizing agent to 4 parts water, and successively coating other articles in said bath while maintaining the bath at a temperature between 120°C and 155°C, and regenerating said bath by the addition of 1/2 pound per 100 square feet of article surface coated and 0.1 to 5.0 pounds for 100 pounds weight of the bath, of an activating salt which changes the positively charged iron resulting from previous operation into a negatively charged radical.

9. Method of oxidizing iron or steel articles which comprises immersing said articles in an aqueous solution of weight 2 to 5 parts alkali and 1/2 to 5 parts nitrite and regenerating said bath by the addition of 1/2 pound per 100 square feet of surface oxidized, of an activating salt which changes the positively charged iron resulting from previous operation into a negatively charged radical.

10. Method of oxidizing iron or steel articles which comprises immersing said articles in an aqueous solution of weight 2 to 5 parts alkali and 1/2 to 5 parts oxidizing agent to 4 parts water and successively oxidizing other articles in said bath while maintaining the bath between 120°C and 155°C, and regenerating said bath by adding 0.1 to 5.0 pounds for 100 pounds weight of the bath of a material adapted to add a cyanide radical to the solution in the bath.

11. Method of oxidizing iron or steel articles which comprises immersing said articles in an aqueous solution of weight 2 to 5 parts alkali and 1/2 to 5 parts oxidizing agent to 4 parts water, and successively oxidizing other articles in said bath while maintaining the bath between 120°C and 155°C, and regenerating said bath by adding 0.1 to 5.0 pounds for 100 pounds weight of the bath of a material adapted to add a tartrate radical to the solution.

12. Method of oxidizing iron or steel articles which comprises immersing said articles in a bath of an aqueous solution of an alkali and an oxidizing agent, and regenerating said bath by adding 0.1 to 5.0 pounds for 100 pounds weight of the bath of a material adapted to add a tannate radical to the solution.

13. Method of coating iron or steel articles which comprises immersing said articles in an aqueous solution of an alkali and an oxidizing agent, and regenerating said bath by adding a cyanide.

14. Method of oxidizing iron or steel articles which comprises immersing said articles for a period of 1/4 to 30 minutes in an aqueous solution of weight 2 to 5 parts alkali and 1/2 to 5 parts oxidizing agent to 4 parts water, and regenerating said bath by adding 0.1 to 5.0 pounds of a cyanide for 100 pounds weight of the bath.

15. Method of coating iron or steel articles which comprises immersing said articles in an aqueous solution of an alkali and a nitrite, and regenerating said bath by adding a cyanide.

16. Method of oxidizing iron or steel articles which comprises immersing said articles in an aqueous solution of an alkali and an oxidizing agent, and regenerating said bath by adding sodium cyanide.

17. Method of coating iron or steel articles, which comprises immersing said articles in an aqueous solution of an alkali and an oxidizing agent, and regenerating said bath by adding sodium cyanide.

18. Method of coating iron or steel articles which comprises immersing said articles in an aqueous solution of sodium hydroxide and sodium nitrite, and regenerating said bath by adding sodium cyanide.

19. Bath for surface treating ferrous articles progressively, comprising an aqueous solution of an alkali and an oxidizing agent which is adapted to cause chemical action to take place on the surface of said articles but which becomes inefficient due to iron ions accumulating from said action, and an activating agent other than said oxidizing agent which prevents said iron ions from interfering with the operation.

20. Bath for surface treating ferrous metal articles comprising an aqueous solution of an alkali and an oxidizing agent other than litharge, and sufficient activating agent differing in chemical composition from either of the two aforesaid substances and capable of forming complex ions with ions of iron, to eliminate inhibiting effect of iron ions resulting from previous operation of the bath.

21. Bath for surface treating ferrous metal articles, an aqueous solution containing by weight 2 to 5 parts alkali and 1/2 to 5 parts oxidizing agent to 4 parts water, regenerated by the addition of 0.1 to 5.0 pounds for 100 pounds weight of the bath, of an activating salt which prevents iron ions resulting from previous operation from interfering with the operation of the bath said activating agent being selected from the group of chemicals known to form complex compounds with iron ions.

22. Bath for coating iron and steel articles, comprising an aqueous solution of an alkali and an oxidizing agent, and sufficient activating salt to change the positively charged iron resulting from previous operation into a negative charged radical, in which said oxidizing agent and said activating salt cooperate to prevent said coating from containing any other metal.

23. Bath for coating iron or steel articles, comprising an aqueous solution containing an alkali, an oxidizing agent of the group consisting of persulphate, peroxide, permanganate, perchlorate, chlorate, nitrate, nitrite, nitrates, nitroso rate of a material selected from the group consisting of sodium, potassium, lithium and barium, and a reviving agent selected from the group of activating agents which form complex compounds with iron ions and prevent inhibiting
action thereof, consisting of a cyanide, cyanate, oxalate, tartrate, lactate, formate and tannate of a metal selected from the group consisting of sodium, potassium and lithium.

24. Bath for coating iron and steel articles, comprising an aqueous solution consisting of by weight 2 to 5 parts alkali and \( \frac{1}{4} \) to 5 parts oxidizing agent other than litharge to 4 parts water, and regenerated by addition of 0.1 to 5.0 pounds for 100 pounds of bath, of an activating salt which changes the positively charged iron resulting from previous operation into a negative charged radical.

25. Bath for coating iron and steel articles, comprising an aqueous solution of an alkali and an oxidizing agent other than litharge, regenerated by addition of a cyanide.

26. Bath for oxidizing iron and steel articles, comprising an aqueous solution of by weight 2 to 5 parts hydroxide and \( \frac{1}{4} \) to 5 parts nitrite to 4 parts water, regenerated by a material selected from the group of materials which form complex ions with iron ions, consisting of cyanides, tannates and tartrates.

27. Bath for coating iron and steel articles, comprising an aqueous solution of an alkali and a nitrite, regenerated by addition of a cyanide.

28. Bath for coating iron and steel articles, comprising an aqueous solution of an alkali and a water soluble oxidizing agent, regenerated by addition of sodium cyanide.

29. Bath for coating iron and steel articles, comprising an aqueous solution of alkali and nitrite of an alkali metal, regenerated by addition of a cyanide of an alkali metal.

30. Bath for oxidizing iron and steel articles, comprising an aqueous solution of by weight 2 to 5 parts hydroxide and \( \frac{1}{4} \) to 5 parts nitrite to 4 parts water, regenerated by addition of 0.1 to 5.0 pounds of cyanide for 100 pounds of bath.

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