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## BRIGHT DIP

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This invention relates to bright-dips for zinc plated articles, and is particularly directed to bright-dips, and to processes of bright-dipping, which employ an acidic aqueous solution containing about two to eight per cent hydrogen peroxide, the aqueous solution having a pH above about one.

In addition to their low cost, electrodeposited zinc coatings display many characteristics which should cause them to be particularly desirable as protective and ornamental finishes. Although zinc is not very resistant to corrosion, it does not accelerate the corrosion of iron or steel as do such metals as copper and nickel. On the contrary, zinc being higher in the electromotive series, will protect iron or steel against rusting even after appreciable areas of the base metal are exposed. Polished zinc metal moreover, has a pleasing metallic lustre with a slightly blue hue.

Despite their numerous advantages over many commonly used coating materials, electrodeposited zinc coatings have not enjoyed the use which they deserve because they do not possess, and even if polished, do not retain a pleasing appearance. The known methods of electroplating zinc almost invariably result in dark, discolored plates. Even when the plates at first have a fairly satisfactory appearance, they soon become dark and discolored. Moreover, the electrodeposited zinc coatings are very susceptible to staining: for instance, when they are touched with the fingers in handling, they are marked and stained by the mere contact.

I have found that the treatment of electrodeposited zinc coatings with certain acidic hydrogen peroxide solutions produce a bright and lustrous finish. This finish displays a passivity to staining, and it may be handled without danger to its appearance. The finish, moreover, is much more resistant to corrosion and tarnishing than untreated electrodeposited zinc coatings. At a low cost I thus obtain a finish which is acceptable in practically any field that requires a protective metallic finish.

The bright dip compositions of this invention are composed of hydrogen peroxide in acidic, aqueous solution. The peroxide concentration may vary widely, but the best results are obtained with from about two to eight per cent  $H_2O_2$ , by weight. The peroxide is used in an acidic solution with a pH above about five-tenths, tho, as will hereafter appear, I prefer to use from about pH 0.5 to pH 3.5 or, more specifically, from about pH 1. to pH 2.5.

Neither the hydrogen peroxide nor the acidic

materials serve alone as a satisfactory bright-dip. Alone, hydrogen peroxide may remove a slight amount of stain, and alone an acidic solution, within the pH range here used, has little effect. Apparently there is some synergetic action between hydrogen peroxide and acidic materials which causes an acidic peroxide solution to exercise an unexpected passivating and brightening action.

The hydrogen peroxide solution may be acidified with any desired material of acid reaction. I prefer to use sulfuric acid, both because it is relatively inexpensive and because it leads to excellent results. I may, however, use inorganic acids such as hydrochloric acid, phosphoric acid, and carbonic acid, or organic acids such as acetic acid, lactic acid, and citric acid. Very weak acids such as carbonic acid and hypochlorous acid are none too satisfactory for, while they operate as do stronger acids, they are effective to a much smaller degree. Some acids, such as hydriodic acid, are not economical because they cause a rather rapid decomposition of the peroxide. While I may use any acid, organic or inorganic, I prefer to use acetic acid or a mineral acid such as sulfuric acid or hydrochloric acid.

Instead of using acids, I may acidify the peroxide solutions with acidulous salts such as ferric chloride, potassium per sulfate, and sodium bisulfate. While any acidulous salt may be employed, certain ones, such as iron or copper salts, are none too satisfactory because they accelerate the decomposition of hydrogen peroxide. It is also noted that, generally, I prefer the bright-dip not to contain a compound the cation of which is a metal below zinc in the electromotive series.

The ratio of hydrogen peroxide to acidic material is of great importance. When sulfuric acid is used as the acidifying material, the hydrogen peroxide ( $H_2O_2$  by weight) to acid ( $H_2SO_4$  by weight) ratio should not be far outside the ratios of four to one and forty-eight to one. If substantially larger or smaller amounts of acid are used, the results obtained are not as satisfactory as may be desired. There are numerous other factors such as cost, stability, etc. which make the above indicated range an optimum.

The hydrogen ion concentration of a given peroxide solution, therefore, must fall within certain limits if the optimum peroxide-acid ratios are to be used. With a two per cent  $H_2O_2$  solution, for instance, the  $H_2SO_4$  content may vary from about one twenty-fourth per cent to about one-half per cent. These limits correspond to a hydrogen ion concentration range of about pH 2.2 to 5.5.

to pH 1.4. With an eight per cent  $\text{H}_2\text{O}_2$  solution, the  $\text{H}_2\text{SO}_4$  content may vary from about one-sixth per cent to about two per cent. These limits correspond to a hydrogen ion concentration range of about pH 1.7 to about pH 1.

The ratio of hydrogen peroxide, considering concentration, to sulfuric acid may be expressed, approximately, in terms of the peroxide concentration (%  $\text{H}_2\text{O}_2$  by weight) by the following range:

$$1. \text{ Bright-dip } \text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} (48 \text{ to } 1 \text{ ratio})$$

$$2. \text{ Bright-dip } \text{pH} \cong \log_{10} \frac{50}{\% \text{H}_2\text{O}_2} (4 \text{ to } 1 \text{ ratio})$$

The first expression is substantially equivalent to saying that the peroxide-sulfuric acid ratio is forty-eight to one, and the second expression substantially equivalent to saying that the peroxide-sulfuric acid ratio is four to one. These expressions thus represent the limits found by experiment. It will be understood that the equations are not mathematically exact definitions of the relationships existing. The pH of a solution is a function of the dissociation constant of the acid at the particular concentration, and in the equations an average dissociation constant is used. The variation from the exact relationship is not great, and, as great exactitude is not required, the definitions are sufficient for my purposes.

Comparing computed pH values with those given above, it is seen that with a two per cent peroxide solution the pH may range from:

$$\text{pH} \cong \log_{10} \frac{360}{2} = 2.2$$

$$\text{to: } \text{pH} \cong \log_{10} \frac{50}{2} = 1.4$$

These values, then, agree with those above given. At a peroxide concentration of eight per cent, the above values are pH 1. to pH 1.7 while the computed values are pH .8 to pH 1.7. The error in the high acid limit of the eight per cent peroxide solution is, therefore, only two-tenths pH, and this is about as great an error as will be encountered.

I prefer that the pH be no lower than pH 1., and expression 2. may be revised to meet this condition as follows:

$$3. \text{ Bright-dip } \text{pH} \cong \log_{10} \frac{80}{\% \text{H}_2\text{O}_2}$$

According to this, the high acid limit for an eight per cent peroxide solution is pH 1., and for a two per cent peroxide solution is pH 1.6.

More specifically I prefer to use a hydrogen peroxide-sulfuric acid ratio of about sixteen to one. This may be expressed for various peroxide concentrations:

$$4. \text{ Bright-dip } \text{pH} \cong \log_{10} \frac{160}{\% \text{H}_2\text{O}_2}$$

A preferred two per cent peroxide solution, then, contains about one-eighth per cent sulfuric acid ( $\text{H}_2\text{SO}_4$  by weight), and it has a pH, according to Equation 4, of about pH 1.9 and its actual pH is about pH 1.82. A preferred four per cent peroxide solution, similarly, contains one-fourth per cent sulfuric acid ( $\text{H}_2\text{SO}_4$  by weight), has a calculated pH of pH 1.6, and has an actual pH of about pH 1.61. A preferred eight per cent peroxide solution, similarly, contains about one-half per cent of sulfuric acid ( $\text{H}_2\text{SO}_4$  by weight), has a

calculated pH of pH 1.3, and has an actual pH of about pH 1.40.

The pH may be determined in any desired manner: for instance, by electrometric methods. It will be readily understood that in measuring the pH of a given solution with color indicators, an acid solution should be made up to the required strength and tested before adding the peroxide. If the peroxide were present, it would tend to bleach and decolorize the indicators and thus falsify the results obtained.

The generalizations above given for sulfuric acid hold to some extent for other acidic materials, and I shall use the approximations of the above equations as one generic mode of expression. A highly ionized acid, hydrochloric acid, operated very satisfactorily with four per cent peroxide and at a pH 1.6 (according to 4).

A weak acid, such as acetic, which is only slightly ionized, does not need to be used in as great a concentration as the pH determined from the above equations would indicate. With a four per cent peroxide solution, the pH values found most practical ranged from about pH 2.95 to about pH 2.68. This amounted to an acetic acid content from about four-tenths to one and five-tenths per cent by weight. The expression 1 may be revived to include such weak, acidic materials within the range from expressions 1 to 2 or 1 to 3, thus:

$$\text{Bright-dip } \text{pH} \cong \log_{10} \frac{4000}{\% \text{H}_2\text{O}_2}$$

Extremely weak acidic materials, such as carbonic acid, cannot be used to obtain a low pH. I include such materials broadly, however, when it is desired merely to use a peroxide solution with a pH above pH 1. or pH 0.5.

It will thus be understood that the above equations and considerations represent approximations, and that some allowances are preferably made according to the specific nature of the acidifying material used, the conditions of use, and other similar factors.

The following specific examples are given more completely to explain my invention:

*Example 1.*—A steel article was zinc plated in known manner in a conventional bath of the following composition:

	Grams per liter
NaOH .....	38
NaCN .....	80
ZnO .....	45
Gelatine .....	1

After the article was zinc plated, it was rinsed in water and then dipped into a bath of the following composition:

Hydrogen peroxide .....	4. % $\text{H}_2\text{O}_2$ by weight
Sulfuric acid .....	0.25 % $\text{H}_2\text{SO}_4$ by weight

After about fifteen seconds the article was satisfactorily bright, and it was then removed from the bright-dip, rinsed in water, and dried.

The bright-dip as above given is one of the best tried. Using the same amount of peroxide, bright-dips were made up using from  $\frac{1}{2}$  to 1 % of  $\text{H}_2\text{SO}_4$  with good results.

*Example 2.*—The process of Example 1 was used but the bright-dip had the following composition:

Hydrogen peroxide .....	2. % $\text{H}_2\text{O}_2$ by weight
Sulfuric acid .....	$\frac{1}{8}$ % $\text{H}_2\text{SO}_4$ by weight

Very good results were obtained. With the same amount of peroxide and from  $\frac{1}{2}$  % to  $\frac{1}{4}$  %

H<sub>2</sub>SO<sub>4</sub>, good results were obtained. The time required satisfactorily to brighten the plates varied from about ten to twenty seconds.

Example 3.—The process of Example 1 was followed with a bright-dip of the following composition:

Hydrogen peroxide..... 8% H<sub>2</sub>O<sub>2</sub> by weight  
Sulfuric acid..... 0.5% H<sub>2</sub>SO<sub>4</sub> by weight

Very good results were obtained. Using the same amount of peroxide, bright-dips using from 1/8 to 2% H<sub>2</sub>SO<sub>4</sub> were tried with good results.

Example 4.—The process of Example 1 was followed with a bright-dip of the following composition:

Hydrogen peroxide..... 4% H<sub>2</sub>O<sub>2</sub> by weight  
Hydrochloric acid..... 0.15% HCl by weight

Excellent results were obtained.

Example 5.—The process of Example 1 was followed with a bright-dip of the following composition:

Hydrogen peroxide..... 4% H<sub>2</sub>O<sub>2</sub> by weight  
Acetic acid..... .6% by weight

Very good results were obtained. Using the same amount of peroxide, bright-dips were tried with from 0.4% to 1.5% acetic acid with good results.

While I have mentioned a specific type of plating bath in the examples, I do not intend to be limited thereby. I may use my bright-dips on articles plated by any method. In general, however, the most satisfactory results are achieved when as smooth and bright a plated article as is obtainable is treated.

As above described, my process includes plating an article, rinsing it, and exposing it to the action of one of my bright-dips. I sometimes find it desirable to interpose an acid dip treatment between the rinsing and bright-dip treatments. By subjecting the plated article to the action of a dilute acid, some foreign materials, such as residues of the plating solution, may be removed. The life of the bright dip may be lengthened, as the plated article carries less material which might tend to decompose the hydrogen peroxide. As an example of this modified procedure I give the following:

Example 6.—A metal article was plated, in conventional manner, in a zinc cyanide bath. The plated article was first rinsed in water and then dipped into a 1/2% solution of C. P. sulfuric acid. After a few moments the article was removed from the dilute acid, rinsed in water, and then exposed to the bright-dip of Example 1. The plated article had an excellent finish. This procedure was repeated until the bright-dip lost its effectiveness. Similarly, following the process of Example 1 until the dip was exhausted, it was found that the use of the preliminary acid dip extended the life of the bright dip almost fifty per cent.

Instead of using sulfuric acid in the preliminary acid dip, I may use solutions of other acids and acidulous salts such as are above enumerated. The concentration of the preliminary acidic dip may be varied widely, but it should not be so concentrated as to etch the zinc finish. The preliminary dip is characterized by containing a substance of acid reaction such as an acid, organic or inorganic, or an acidulous organic or inorganic salt. I prefer, however, to use dilute sulfuric acid.

I may, if desired, omit either, or both of the rinsing treatments. If the second rinsing treat-

ment is omitted, a small amount of acid will be carried into the bright dip with each article. Care must be exercised, in this case, lest the bright-dip become too strongly acid.

My bright-dip has a relatively long life, but care must be exercised lest some agent or condition be encountered which will accelerate decomposition.

I prefer to use relatively pure acids, because impurities such as are commonly found in commercial acids may cause decomposition of the bright-dip. The solution is preferably shipped and used in glass, glazed stoneware, hard rubber, or stainless steel receptacles. If lead, Monel metal, fiber, and similar materials are used to contain my peroxide bright-dip, a more rapid decomposition occurs.

I may, if desired, add a small amount of a known stabilizer for peroxide. The nature and use of stabilizers is well known to the trade and need not be described in detail. I have found small amounts of alcohol, sodium pyrophosphate and sodium stannate, glycerine, etc. quite satisfactory.

The peroxide dip may be sold in the form of a relatively concentrated solution of peroxide and acidulous material and a buyer can dilute the product to the desired extent. Of course, it can be sold as a relatively dilute solution or it can be made up at the place of use.

While I have shown certain specific composition and processes, I do not intend to be limited thereby, the scope of my invention appearing from the following claims.

I claim:

1. A bright-dip for zinc comprising an acidic hydrogen peroxide solution with a pH from about pH 0.5 to pH 3.5.

2. A bright-dip for zinc comprising an acidic hydrogen peroxide solution with a pH from about pH 1 to pH 2.5.

3. A composition for passivating and brightening an electrodeposited zinc coating, comprising hydrogen peroxide and an acid, the peroxide amounting to about two to eight per cent by weight, and the composition having a pH of the order of

$$\text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{50}{\% \text{H}_2\text{O}_2}$$

4. a composition for passivating and brightening an electrodeposited zinc coating, comprising hydrogen peroxide and acetic acid, the composition containing about two to eight per cent of peroxide, and the composition having a pH of the order of

$$\text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{80}{\% \text{H}_2\text{O}_2}$$

5. A composition for passivating and brightening an electrodeposited zinc coating, comprising hydrochloric acid, the composition containing about two to eight per cent of peroxide, and having a pH of the order of

$$\text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{50}{\% \text{H}_2\text{O}_2}$$

6. A composition for passivating and brightening an electrodeposited zinc coating, comprising hydrogen peroxide and sulfuric acid, the ratio of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> being from about forty-eight-to-one to four-to-one, and the composition containing about two to eight per cent H<sub>2</sub>O<sub>2</sub>.

7. A composition for passivating and brightening an electrodeposited zinc coating, compris-

ing about four per cent of hydrogen peroxide and about one-fourth of a per cent of sulfuric acid.

8. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising an acidic hydrogen peroxide solution, the bright dip having a pH no lower than about pH 0.5.

9. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising an acidic hydrogen peroxide solution with a pH from about pH 0.5 to pH 3.5.

10. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising an acidic hydrogen peroxide solution with a pH from about pH 1. to pH 2.5.

11. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising an acidic hydrogen peroxide solution which has a pH of the order of

$$\text{pH} \cong \log_{10} \frac{4000}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{50}{\% \text{H}_2\text{O}_2}$$

12. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising an acidic hydrogen peroxide solution which contains about two to eight per cent peroxide which has a pH of the order of

$$\text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{50}{\% \text{H}_2\text{O}_2}$$

13. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising an acidic hydrogen peroxide solution which contains about two to eight per cent peroxide, and which has a pH of the order of

$$\text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{80}{\% \text{H}_2\text{O}_2}$$

14. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising hydrogen peroxide and acetic acid, the bright dip containing about two to eight per cent of peroxide, and the bright dip having a pH of the order of

$$\text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{80}{\% \text{H}_2\text{O}_2}$$

15. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising about four per cent of hydrogen peroxide, and

about four-tenths to one and five-tenths per cent of acetic acid.

16. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising hydrochloric acid, the bright dip containing about two to eight per cent of peroxide, and having a pH of the order of

$$\text{pH} \cong \log_{10} \frac{360}{\% \text{H}_2\text{O}_2} \text{ to } \text{pH} \cong \log_{10} \frac{50}{\% \text{H}_2\text{O}_2}$$

17. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising hydrogen peroxide and sulfuric acid, the ratio of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{SO}_4$  being about forty-eight-to-one to four-to-one.

18. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising hydrogen peroxide and sulfuric acid, the ratio of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{SO}_4$  being from about forty-eight-to-one to four-to-one, and the composition containing about two to eight per cent  $\text{H}_2\text{O}_2$ .

19. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising about two to eight per cent of hydrogen peroxide and the quantity of sulfuric acid required to make the  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{SO}_4$  ratio about sixteen to one.

20. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising about four per cent of hydrogen peroxide and about one-fourth of one per cent of sulfuric acid.

21. In a process of passivating and brightening an electrodeposited zinc coating, the steps comprising subjecting an electrodeposited coating to the action of a dilute acidic solution, and subsequently subjecting the article to the action of a bright dip comprising an acidic hydrogen peroxide solution having a pH of no lower than about pH 0.5.

22. In a process of passivating and brightening an electrodeposited zinc coating, the steps comprising subjecting the electrodeposited coating to the action of a dilute sulfuric acid solution, and subsequently subjecting the article to the action of a bright dip comprising hydrogen peroxide and sulfuric acid, the ratio of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{SO}_4$  being from about forty-eight-to-one to four-to-one, the composition containing about two to eight per cent  $\text{H}_2\text{O}_2$ .

23. In a process of passivating and brightening an electrodeposited zinc coating, the step comprising subjecting the electrodeposited coating to the action of a bright dip comprising a solution of hydrogen peroxide and sulfuric acid, the bright dip having a pH no lower than about pH 0.5.

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