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Patented Apr. 18, 1939

2,154,455

UNITED STATES PATENT OFFICE

2,154,455

CADMIUM BRIGHT DIP

Raymond J. Kepfer, Lakewood, Ohio, assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application February 8, 1934, Serial No. 710,225

7 Claims. (Cl. 148—6)

This invention relates to hydrogen peroxide solutions which contain a substance of acid reaction and to their use as bright dips for cadmium plated articles.

The cadmium plating processes now in use frequently product plated articles which are stained and which are not of a uniformly bright finish. With articles of very irregular shape some areas may be somewhat dull so that the piece does not have as uniformly a bright and lustrous finish as is desirable.

It has been proposed to dip the plated articles in solutions of dilute oxidizing acids, but while a fairly uniform finish is thus obtained, much of the cadmium is dissolved and the plating may be seriously damaged. If the solution of oxidizing acid be dilute enough not to injure the plating, it is ineffective as a bright dip.

I have found that a hydrogen peroxide solution which contains a substance of acid reaction serves as a very satisfactory bright dip for cadmium plated articles. My bright dip acts upon cadmium plated articles to give them a lustrous, uniformly bright finish free from stains and discoloration.

Plated articles may be left in the bath for a fairly long time without substantial damage to the plating. This offers a great advantage over the use of the previously proposed oxidizing acid dips wherein the plating is dissolved with relatively great rapidity.

One especially beneficial effect of my bright dips is that cadmium plated articles which have been brightened according to my invention subsequently show a resistance to stains such as are produced by handling. If a cadmium plated article which has not been bright dipped is touched by the fingers, stains are left at the points of contact. It is, of course, very difficult to handle such plated articles without injuring their finish. Articles which have been bright dipped according to my invention may be handled freely without injury to their finish.

Another advantage of my bright dip is that the brightened plate may be readily plated with other metals such as nickel. Prior to nickel plating iron or steel it is sometimes desirable to plate the iron with cadmium. If the cadmium plated iron or steel is bright dipped in certain oxidizing acid dips, a subsequent nickel plate will not adhere properly. If the cadmium plated iron or steel is bright dipped in my bright dip, a subsequent nickel coat adheres in a very satisfactory manner.

I have also found that cadmium plated articles which have been dipped in a solution of acidified hydrogen peroxide are easily washed or rinsed after the dipping. This is not true of some other oxidizing acid bright dips which form a colored film which requires considerable washing to effect complete removal.

While an acidified hydrogen peroxide solution constitutes an excellent bright dip, hydrogen peroxide in neutral or alkaline solution does not have a satisfactory brightening action though it may sometimes remove a slight amount of stain. Likewise, the acidifier alone may remove some stain but it does not serve as a brightener in a satisfactory manner.

The following examples are given to explain more fully the practice of my invention:

Example 1.—A metal sheet bent to U-form was cadmium plated in a conventional manner. The use of a U-form article closely approximates commercial plating conditions and the article is not uniformly bright, being duller in the recessed portion. The plated article was rinsed free of the plating solution in cold water and then dipped for about fifteen seconds at room temperature in a bright dip consisting of 9 ounces of a 30% (by weight) hydrogen peroxide solution, two-third of an ounce of 66° Bé. C. P. sulfuric acid and a gallon of water. After removing the plated article from the bright dip it was carefully washed and dried. The resulting plated sheet had a lustrous, uniformly bright finish, the recessed portions being uniform in appearance with the rest of the article.

I prefer to use a pure acid as impurities such as are commonly found in commercial acids might cause decomposition of the peroxide.

The ratio of H_2O_2 (by weight) to H_2SO_4 (by weight) is of great importance. In fact, it appears to be more important than the peroxide concentration. As the acid is increased and the H_2O_2/H_2SO_4 ratio falls to one to one or below, the plate becomes white and as the ratio drops further becomes gray or black. The discoloration by the dip, with a ratio of substantially below one to one, is typical of a direct acid etch. This ratio is dependent to some extent upon the actual concentration involved, a higher peroxide ratio being required in the more dilute solutions. For example, fair results were obtained using 2% H_2SO_4 and 2% H_2O_2 by weight, but 0.2% of each gave poor results. Good brightening can be obtained, however, by using 0.5% H_2O_2 and 0.2% H_2SO_4. My preferred H_2O_2/H_2SO_4 ratio is about four to one. With higher ratios the brightening action is more vigorous, but the stability of the dip is not quite as great and the cost is increased.

The concentration of either the peroxide or the acid, or both, in the dip may be decreased or increased so long as the ratio of peroxide to acid does not become too low, the effect being to increase or decrease the time required to obtain a satisfactory bright finish.

Example 2.—The procedure of Example 1 was followed, using as a bright dip one gallon of water containing three per cent by weight of 23° Bé. hydrochloric acid and two per cent by weight H_2O_2. The finish of the plated article was much improved.

Example 3.—The procedure of Example 1 was followed using a water solution containing 5% lactic acid and 2% hydrogen peroxide, by weight, as the bright dip. Again the appearance of the U-shaped cadmium plated article was greatly improved, the recessed portions being uniformly bright and lustrous with the rest of the piece.

While I have listed only sulfuric, hydrochloric, and lactic acids in the above examples, I do not intend to be limited thereto. I may use any soluble acid, organic or inorganic. Very weak acids such as carbonic and hypochlorous acids are not preferred, for while they operate in the same manner as stronger acids, they are effective to a much smaller degree. Some acids, such as hydriodic acid, cause a rather rapid decomposition of the perioxide and the life of the dip is rendered very short. Dips using such acids are not as economical as are dips using more stable acids. As other examples of acid which may be used I mention acetic, citric, and phosphoric with which very satisfactory bright dips were made.

Instead of using an acid to acidify the peroxide solution, I may use acidulous organic and inorganic salts, such as ferric chloride, cupric sulfate, potassium persulfate, cupric chloride, sodium bisulfate, potassium acid phthalate, etc. Although any of these salts and many others when used with hydrogen peroxide will give some brightening action, I do not prefer to use acidulous salts of the heavy metals such as iron or copper since they cause very rapid decomposition of the peroxide. A specific example of the use of a salt is given below.

Example 4.—The procedure of Example 1 was followed, using as a bright dip one gallon of water containing five per cent by weight potassium persulfate, and two per cent by weight of H_2O_2. The plated article was satisfactorily brightened by immersion in the dip.

In all the above examples the solutions are rather dilute, both with respect to peroxide and acidic constituent content. They may, if desired, be more or less concentrated. If a more concentrated dip is used the time required to brighten the plated article is less. In other words, the concentration of either constituent or both may be changed within certain limits so long as the ratio of peroxide to acidic constituent does not become too low. This satisfactory ratio varies with acids of different properties, especially different acidic strengths, a higher proportion of weaker acid being required.

While I may use any material of acid reaction to acidify the peroxide solutions, I prefer to use mineral acids, organic acids or alkali metal salts which when dissolved in water form acid solutions. Specifically, sulfuric acid is the best acidifier from the standpoint of results obtained, cost, stability of the solution, etc.

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 5.—A metal article was plated, in conventional manner, in a cadmium cyanide bath. The plated article was first rinsed in water and then dipped into a 1% 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 a preliminary sulfuric 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 cadmium 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 to use dilute sulfuric acid.

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

I claim:

1. A bright dip for cadmium comprising hydrogen peroxide and sulfuric acid, the ratio of peroxide to acid being about four to one.

2. In a process of brightening cadmium, the step comprising contacting the cadmium with a bright dip comprising hydrogen peroxide and sulfuric acid, the ratio of peroxide to acid being about four to one.

3. In a process of brightening cadmium, the steps comprising subjecting the plated article to the action of a preliminary bath substantially free from oxidizing agents which contains a substance of acid reaction, and exposing the cadmium to a bright dip which comprises a hydrogen peroxide solution and a substance of acid reaction.

4. In a process of brightening cadmium, the steps comprising exposing the cadmium to the action of a preliminary bath substantially free from oxidizing agents which comprises a mineral acid, and exposing the cadmium to a bright dip which comprises hydrogen peroxide and a mineral acid.

5. In a process of brightening cadmium, the steps comprising exposing the cadmium to the action of a preliminary bath substantially free from oxidizing agents which comprises sulfuric acid, and exposing the cadmium to a bright dip which comprises hydrogen peroxide and sulfuric acid.

6. In a process of brightening cadmium, the steps comprising exposing the cadmium to the action of a preliminary bath substantially free

from oxidizing agents which comprises sulfuric acid, and exposing the cadmium to a bright dip which comprises hydrogen peroxide and sulfuric acid, the ratio of peroxide to acid in the bright dip being no less than about two and one-half to one.

7. In a process of brightening cadmium, the steps comprising exposing the cadmium to the action of a preliminary bath substantially free from oxidizing agents which comprises sulfuric acid, and exposing the cadmium to a bright dip which comprises hydrogen peroxide and sulfuric acid, the ratio of peroxide to acid in the bright dip being no less than about four to one.

RAYMOND J. KEPFER.