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[54] **STABILIZED ACIDIC HYDROGEN PEROXIDE SOLUTIONS**

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[58] **Field of Search** 252/186, 95, 97, 99, 100, 252/135, 157, 142; 423/272, 273, 584

[56] **References Cited**

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[57] **ABSTRACT**

Stabilizers are provided which control copper ion-catalyzed degradation of hydrogen peroxide. In pickling baths the H_2O_2 concentration may be up to about 50% by weight, in the presence of strong inorganic nonoxidizing acids at up to about 50% by weight, and at temperatures of up to about 90°C. Such stabilizers are included in concentrations of up to about 1.5% by weight. The stabilizers, at concentrations of up to about 5% by weight, may also be formulated into H_2O_2 of up to 80% concentration by weight. The stabilizers are selected from the group consisting of adipic acid, glutaric acid, succinic acid, their methyl derivatives, salts, and mixtures of them.

23 Claims, No Drawings

STABILIZED ACIDIC HYDROGEN PEROXIDE SOLUTIONS

BACKGROUND OF THE INVENTION

Articles of copper or copper alloys are generally cleaned in an operation known as pickling by treatment with a mineral acid solution containing an oxidizing agent. The function of the oxidizing agent is to oxidize cuprous oxide scale and smut to the cupric form, in which valence state it is soluble in the pickling acid, usually sulfuric acid. The oxidizing agent commonly used has been sodium dichromate. However, because of the unacceptability of that chemical from the pollution standpoint, hydrogen peroxide is finding acceptance as the oxidizer.

It is well known, however, that copper ions catalyze the decomposition of hydrogen peroxide in acid medium, particularly at the elevated temperatures used for pickling baths. Thus, there has been a continuing search for materials which will stabilize H_2O_2 under pickling conditions. Among the materials suggested have been urea (German Pat. No. 1,255,443), fatty acids (British Pat. No. 1,119,969, French Pat. No. 1,468,442, and U.S. Pat. No. 3,537,895), saturated aliphatic alcohols (French Pat. No. 1,539,960), glycerin (U.S. Pat. No. 3,345,225), certain phenols and unsaturated alcohols (U.S. Pat. No. 3,649,194), and phosphoric acid (U.S. Pat. No. 3,373,113).

SUMMARY OF THE INVENTION

According to the present invention there are provided stabilizers selected from the group consisting of succinic, glutaric, and adipic acids, salts, methyl derivatives, and mixtures thereof, which stabilize against copper ion-induced degradation of H_2O_2 in acidic oxidizing solutions at temperatures up to about 90°C. The copper ions (primarily in the cupric form) may be present in concentrations of up to about 5% by weight. The stabilizers will function in any nonoxidizing mineral acid, sulfuric acid being the most commonly employed. The acid concentration may range from about 0.01 to 50% by weight, preferably about 2 to 25% by weight. The H_2O_2 may be present in concentrations from about 0.01 to 80% by weight. These stabilizers may be formulated with H_2O_2 and acid to form an aqueous, acidic oxidizing solution, or may preferably be included in the concentrated aqueous H_2O_2 solution, as commercially prepared and sold, prior to adding the H_2O_2 to the pickling bath.

DETAILED DESCRIPTION OF THE INVENTION

It has now been found that copper ion-induced or catalyzed decomposition of H_2O_2 in aqueous acidic medium at elevated temperatures can be controlled by the addition of stabilizing amounts of succinic, glutaric, or adipic acids, their mono-, di-, or trimethyl derivatives, their salts, or mixtures of them. The effectiveness of the stabilizer is greater the longer the chain length, i.e., adipic acid is the most effective and succinic acid is least effective. The stabilizers may be used in any appropriate concentration; however, if the stabilizer is to be formulated into concentrated H_2O_2 prior to addition to the pickling bath, the solubility of the stabilizer in concentrated H_2O_2 may be the controlling factor. For example, the solubility of adipic acid in 35% H_2O_2 is only about 1% by weight. In pickling baths some stabilizing effect will be seen with as little as 0.003% stabilizer concentration. The usual concentration range in pickling baths will be about 0.015 to 1.5%, preferably about 0.03 to 0.1%. Mixtures of the stabilizers may also be used. Since adipic acid is the most effective, a mixture would preferably include it, attention being paid to the solubility considerations already noted. A particularly preferred mixture is the ratio of about 2 parts of succinic acid to 1 part of adipic acid.

In commercial operations it will be found particularly convenient if the stabilizer is incorporated into the concentrated aqueous H_2O_2 as available commercially. Such a solution can be readily formulated by the H_2O_2 manufacturer to contain at least 0.05% and as much as 5% by weight stabilizer, depending on the solubility of the stabilizer and the concentration of the H_2O_2.

While the stabilizers of this invention will be effective in any strong, nonoxidizing mineral acid solution, sulfuric acid is of most commercial significance. It may also be noted that Caro's acid, an equilibration product of H_2SO_4 and H_2O_2, may be present in the stabilized solution without detracting from the usefulness of the stabilizers. The H_2SO_4 concentration of a pickling bath usually is in the range of about 2 to 25% by weight, preferably 4 to 6%. Other nonoxidizing mineral acids may also be used in these concentration ranges. Such other mineral acids would include hydrochloric, hydrofluoric and phosphoric, such acids being used in the pickling of such metals as iron and aluminum and their alloys.

Hydrogen peroxide concentration in a pickling bath typically ranges from about 0.05 to 15% by weight, preferably 0.5 to 3%, although concentrations as low as 0.01% and as high as 50% may be used. If the stabilizer is formulated into concentrated aqueous H_2O_2, the H_2O_2 concentration may range from about 20 to 80% by weight, preferably about 30 to 70%, more preferably about 35 to 50%. While the stabilizers of this invention may be added directly to H_2O_2 of 70% or greater concentration, this is not recommended since solubility is lessened and there is the possibility of forming peroxyacids. If it is desired to start with, say, 70% H_2O_2, the preferred procedure would be to dissolve the stabilizer in sufficient water that when added to the 70% H_2O_2 the overall H_2O_2 concentration would be reduced to a more easily handled concentration, say, 50%. Even when the stabilizer is to be added to 50% or less H_2O_2, it is still preferred to dissolve the stabilizer in water before addition to the H_2O_2. Any commercially available grade of H_2O_2 may be used in this invention. The H_2O_2 may be unstabilized or preferably may contain any of the usual stabilizing chemicals, e.g., sodium stannate, sodium pyrophosphate, fluosilicates, magnesium sulfate coupled with an alkylidene diphosphonic acid (as taught by U.S. Pat. No. 3,687,627), as well as sodium nitrate and other additives. When present in concentrated commercial H_2O_2 solutions, the concentrations in percent by weight of the more common stabilizers are as follows: stannates, 0.001–1.0%, preferably 0.015–0.07%; pyrophosphates, 0.01–5.0%, preferably 0.05–4.0%; nitrates, 0.001–0.05%, preferably 0.0015–0.04%. An alkylidene diphosphonic acid will preferably be present in a concentration of at least 0.1% by weight.

The stabilizers of this invention will effectively control copper catalyzed decomposition of H_2O_2 at temperatures up to about 90°C. However, in most uses the typical temperature range would be about 15° to 40°C.

The invention is illustrated by the following examples, in which percentages are by weight.

EXAMPLE 1

This example illustrates the stabilizing effect of the acids of this invention.

A solution having the following composition was prepared:

15.0%	H_2SO_4
2.0	$CuSO_4.5H_2O$
2.9	H_2O_2

This solution was then divided and formulated with stabilizer additive and stability of the H_2O_2 at 120°F. was determined, with the following results. Decomposition of H_2O_2 was measured by the standard potassium permanganate titration test.

Table I

Additive	Residual H_2O_2, %			
	2.5 hrs.	5 hrs.	24 hrs.	70 hrs.
None (control)	85	66	—	6
0.5% adipic acid	100	96	—	71
0.2% succinic acid	98	97	81	49
0.5% succinic acid	99	98	90	49
0.17% adipic acid + 0.33% succinic acid	100	99	95	68

EXAMPLE 2

Table II illustrates the effect of pH when a stabilizer of the invention is added to standard commercial concentrated H_2O_2. The H_2O_2 grades used were:

Sample A — Du Pont's Albone (regular), 35% concentration

Sample B — Du Pont's Albone (cosmetic grade), 35% concentration

In Samples A and B the pH of 3.5 was obtained by addition of a sodium hydroxide solution. Samples C and D are the same as A and B, respectively, except that no pH adjustment was made. Sample E was the same as C except that the pH was adjusted by addition of H_3PO_4.

A pH of about 1.5 is that obtained naturally by addition to 35% H_2O_2 of about 3% of the acids of this invention. Whereas commercial concentrated H_2O_2 is typically sold at a pH of about 3.5, Table II shows that it is not desirable to adjust pH to this value after addition of the acid stabilizers. Stability will be optimized by allowing the pH to remain at its natural level.

Table II

3% Succinic Acid in 35% H_2O_2		
Sample	pH	% Loss (20 hrs. at 150°F.)
A	3.5	5.0
B	3.5	3.2
C	1.5	2.0
D	1.5	0.6
E	1.0	>2.0

A peroxide loss of about 2% or less is considered commercially satisfactory.

I claim:

1. An aqueous, acidic, oxidizing solution stabilized against copper ion-catalyzed degradation at temperatures of up to about 90°C. containing about 0.01 to 50 percent hydrogen peroxide by weight, a strong inorganic acid at a concentration of about 0.01 to 50 percent by weight, and a stabilizing amount of a stabilizer selected from the group consisting of adipic acid, glutaric acid, succinic acid, and mixtures thereof.

2. The solution of claim **1** wherein the stabilizer concentration is about 0.003 to 1.5 percent by weight.

3. The solution of claim **2** wherein the stabilizer concentration is about 0.015 to 1.5 percent by weight.

4. The solution of claim **3** wherein the stabilizer concentration is about 0.03 to 0.1 percent by weight.

5. The solution of claim **1** wherein the acid concentration is about 2 to 25 percent by weight.

6. The solution of claim **1** wherein the H_2O_2 concentration is about 0.05 to 15 percent by weight.

7. The solution of claim **6** wherein the H_2O_2 concentration is about 0.5 to 3.0 percent by weight.

8. The solution of claim **1** wherein the stabilizer is adipic acid.

9. The solution of claim **1** wherein the stabilizer is glutaric acid.

10. The solution of claim **1** wherein the stabilizer is succinic acid.

11. The solution of claim **1** wherein the stabilizer is a mixture of the stabilizers.

12. The solution of claim **11** wherein the mixture comprises succinic and adipic acids.

13. The solution of claim **12** wherein the ratio of succinic acid to adipic acid is approximately 2:1 by weight.

14. A concentrated, aqueous, acidic solution of hydrogen peroxide stabilized against copper ion-catalyzed degradation by a stabilizing amount of a stabilizer selected from the group consisting of adipic acid, glutaric acid, succinic acid, and mixtures thereof.

15. The solution of claim **14** wherein the hydrogen peroxide concentration is about 30 to 70 percent by weight.

16. The solution of claim **15** wherein the hydrogen peroxide concentration is about 35 to 50 percent by weight.

17. The solution of claim **14** wherein the stabilizer is adipic acid.

18. The solution of claim **14** wherein the stabilizer is glutaric acid.

19. The solution of claim **14** wherein the stabilizer is succinic acid.

20. The solution of claim **14** wherein the stabilizer is a mixture of the stabilizers.

21. The solution of claim **20** wherein the mixture comprises succinic and adipic acids.

22. The solution of claim 21 wherein the ratio of succinic acid to adipic acid is approximately 2:1 by weight.

23. The solution of claim 14 which contains in addition one or more stabilizing chemicals selected from the group consisting of stannates, sulfates, pyrophosphates, fluosilicates, nitrates, and alkylidene diphosphonic acid.

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