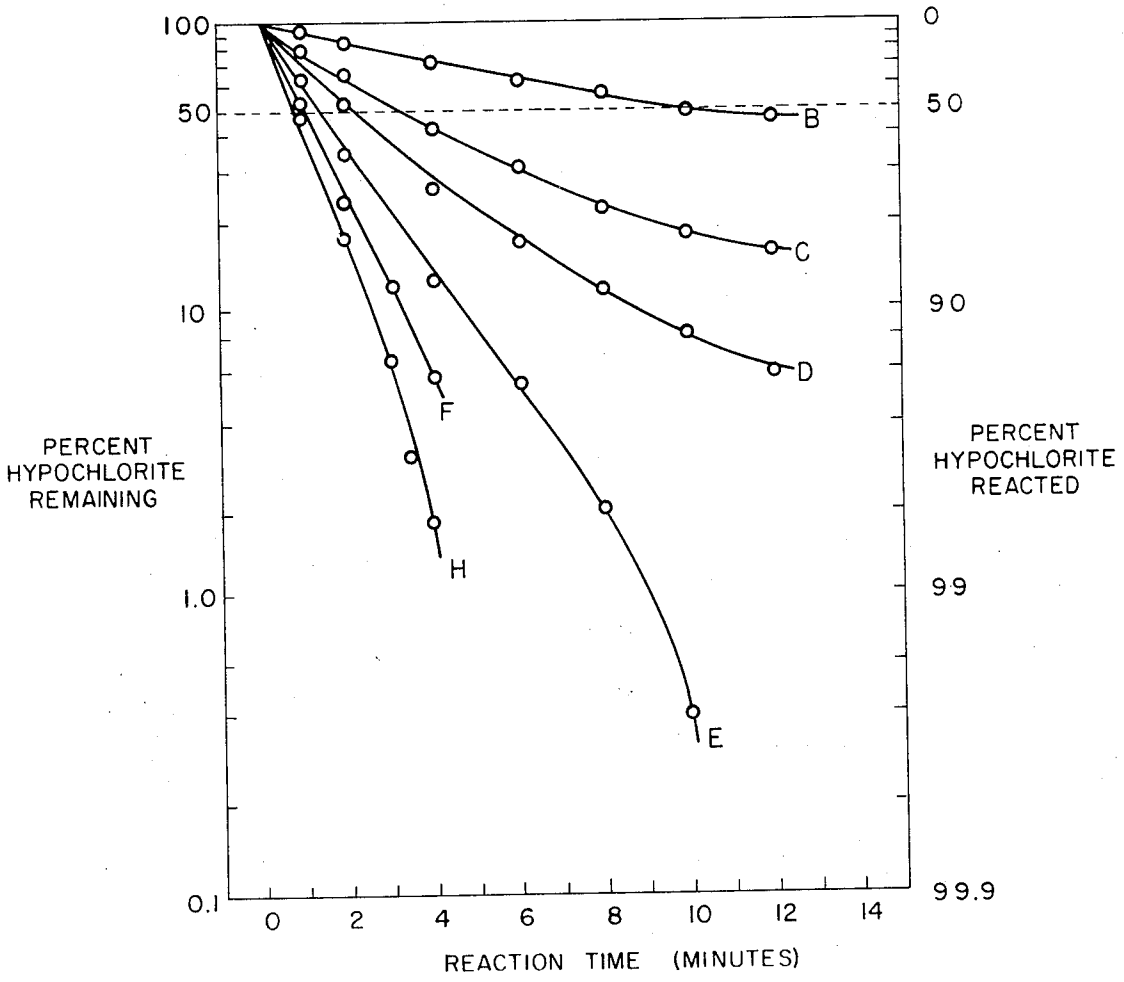
Feb. 20, 1973 W. H. ECHOLS ET AL **3,717,580**

METHOD OF DISINFECTING AND SELF-LIMITING SOLUTION THEREFOR

Filed Dec. 2, 1969

THE HYPOCHLORITE-CITRATE REACTION
KINETIC DATA AT pH 7.0 AND 23°-24° C



INITIAL CONCENTRATIONS

SOLUTION	HYPOCHLORITE	CITRATE
B	0.015 M	0.007M
C	"	0.021
D	"	0.035
E	"	0.063
F	"	0.091
H	"	0.105

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METHOD OF DISINFECTING AND SELF-LIMITING SOLUTION THEREFOR

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ABSTRACT OF THE DISCLOSURE

A solution containing an inorganic hypochlorite salt and an inorganic salt of a hydroxy carboxylic acid and optionally containing an acid to adjust the pH to 4.5–8 and/or a detergent, which disinfects sensitive materials without harming the material by remaining active for a short period of time due to a self consummation feature of the solution.

BACKGROUND OF THE INVENTION

This invention generally relates to the art of disinfecting and more particularly to disinfecting with an aqueous hypochlorite solution which retains its germicidal activity for a relatively short time.

Hypochlorite solutions have been used for many years as germicides, sporicides, virucides and chemical warfare decontaminants. However, their prior use has been generally limited to terrain, heavy construction materials and other items resistant to the inherent corrositivity of hypochlorites. When used on more sensitive materials such as clothing fabrics, one or very few applications could be tolerated. The human body has always been considered too sensitive a material for routine or repeated disinfection or decontamination by hypochlorite solution. Thus, when it was desired to disinfect or decontaminate hypochlorite sensitive materials it has been necessary to use less powerful disinfection or decontamination agents thereby reducing the effectiveness thereof.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide a method of disinfecting or decontaminating sensitive materials using a new aqueous hypochlorite containing composition.

Another object of this invention is to provide a new aqueous hypochlorite containing disinfectant solution.

A still further object of this invention is to provide hypochlorite containing solutions which remain germicidally active for a short period of time.

Another object of this invention is to provide hypochlorite containing solutions which self-destruct.

These and other objects of this invention are accomplished by providing an aqueous disinfectant solution containing an inorganic hypochlorite salt and an inorganic salt of a hydroxy carboxylic acid.

BRIEF DESCRIPTION OF THE DRAWING

Other objects and many of the attendant features of the present invention will be readily appreciated as the same becomes better understood by reference to the solitary drawing which is a graphical illustration of the percent hypochlorite remaining unreacted as the time increases for six different solutions containing varying amount of citrate ion.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The disinfecting solution of this invention comprises an inorganic hypochlorite salt and an inorganic salt of a hydroxy carboxylic acid and can optionally contain some acid to adjust the pH and/or a detergent or detergent mixture.

To obtain reasonably good disinfection the inorganic hypochlorite salt should be present in the solution in an amount sufficient to give a hypochlorite ion concentration of at least about 0.015 M and, for most uses, a concentration of 0.015 M is sufficient although higher concentration may be used if desired. The preferred salts are sodium, calcium and lithium because these are the most readily available inorganic hypochlorite salts. However, any inorganic hypochlorite may be used without affecting the disinfectant qualities of this solution since it is generally known that the hypochlorite ion is the source of the active disinfecting agent and not the cation.

It is preferable, but not necessary, to also add a detergent or detergent mixture to the disinfecting solution for the purpose of enhancing wetting. Any anionic or non-ionic surfactant may be used for this purpose but one should not use cationic surfactants. Generally, the detergent may be present in about 0.05% by weight but, in any event, the amount used is not critical.

Additionally, an acid is preferably added to the solution in order to adjust the pH to a value of between 6.5 and 7.5. The commercially available hypochlorite solutions are quite alkaline having a pH of about 10.-5–11. It is generally believed that hypochlorous acid is the germicidal component in all hypochlorite solutions, but it is present in only very small amounts at high pH values. At a pH of about 7, however, about three-fourths of the hypochlorite is present as hypochlorous acid and only about one-fourth as hypochlorite ion. To be more specific, for the same amount of total available chlorine, the concentration of hypochlorous acid has been found to be about 3,000 times as large at pH 7 as at pH 10.5. Thus, the alkaline hypochlorite solution can be activated by the addition of any acid which is stronger than hypochlorous acid, such as citric acid or sodium dihydrogen phosphate. Thus, while good germicidal activity is attained between pH 4.5 and 8 the optimum pH is 6.5 to 7.5. Table I is a compilation of the relative concentrations of hypochlorus acid and hypochlorite ion in water at 25° C. at various pH values based on $Ka=4.0\times10^{-8}$.

TABLE I

pH	Percent of total oxidizing chlorine as— OCl-	HOCl	Ratio of HOCl/OCl-
11	99.97	0.026	0.00026
10	99.7	0.26	0.0026
9	97.4	2.6	0.026
8	79	21	0.26
7.4	50	50	1.0
7	27	73	2.7
6.5	9	91	10
6	4	96	24
5	0.4	99.6	250

For the purpose of retaining the most desirable pH of 6.5 to 7.5 weak acids are preferred since in addition to acidifying the solution they also act as buffers to keep the pH near a magnitude of 7.

The inorganic salt of the hydroxy carboxylic acid is the constituent in the solution of this invention which brings about the self-limiting character of the solution. Since the hypochlorite will oxidize this constituent and very little reaction is present during the first few seconds of contact it is possible for the hypochlorite to disinfect for a short period of time and then to be neutralized in situ. Although any inorganic salt of hydroxy containing carboxylic acids will work the inorganic salts of citric acid (e.g. sodium citrate) and malic acid have been found preferable. Thus, when a solution contains 0.015 M hypochlorite ion and 0.007 M citrate ion the half-life is about

10 minutes. The solitary drawing shows a number of curves indicating the half-lives of a number of solutions which have varying concentrations of citrate ion. In order for the solutions of this invention to be practically useful, it is desirable that the half-life not exceed 10 minutes so the ratio of hypochlorite concentration to citrate ion concentration will be, at most, about 2:1. It will be obvious to one skilled in the art that as the half-life is decreased the citrate ion concentration goes up and the ratio becomes smaller, e.g. 1:1 or 1:3 etc.

Typical formulations by weight of a self-limiting hypochlorite solution are as follows:

	Percent
Calcium hypochlorite	0.2
Triton X–100 (Rohm and Haas) (non-ionic detergent)	0.05
Sodium citrate	1
Acid:	
Citric	0.2
Or NaH_2PO_4	0.5

Since the above solutions will rapidly lose their disinfectant properties it is generally desirable to add the hypochlorite solution to the solution containing the inorganic salt of a hydroxy carboxylic acid either alone or with a detergent and/or an acid immediately before use. This may be achieved by merely mixing the two solutions or by spraying whereby two streams, one containing the hypochlorite and the other containing the salt of the hydroxy carboxylic acid are mixed in the nozzle of the sprayer.

The solutions of this invention have been used to simultaneously decontaminate a man and all items of this clothing which were contaminated with spores of *Bacillus subtilis* var. *niger*, considered to be equal in decontamination resistance to spores of the extremely resistant anthrax bacillus. Thus, the shirt, trousers, hood, socks, shoes, underwear, mask and the man, himself, were decontaminated by spraying the fully clothed man. The various clothing items were assayed for residual spores by agitating with an extraction solution in plastic bags. Shoes and mask were sectioned after decontamination and the parts separately assayed to determine whether some areas of these items were especially difficult to decontaminate. Sampling of the man's skin for residual contamination was done by ultrasonic agitation of a reservoir of extraction solution in contact with the skin. The results showed an effectiveness of 99.9% or better on all items. Additionally, an AM-FM transistor radio, a typewriter, an electric drill and other materials were also decontaminated using the above solution. These materials still functioned properly after decontamination and showed no ill effects from contact with the hypochlorite solution.

What is claimed is:

1. A method of disinfecting relatively sensitive articles comprising contacting said articles with a solution formed by mixing immediately before use an aqueous solution of an inorganic hypochlorite salt and an aqueous solution of an inorganic salt of a hydroxycarboxylic acid selected from the group citric acid and malic acid, wherein the molar ratio of said hypochlorite salt to said hydroxycarboxylic acid salt is at most 2:1.

2. The method of claim 1 wherein the mixed solution additionally contains an acid to adjust the pH to 4.5–8.

3. The method of claim 2 wherein the mixed solution additionally contains a nonionic or anionic detergent.

4. The method of claim 3 wherein said inorganic hypochlorite is selected from the group consisting of sodium hypochlorite, calcium hypochlorite and lithium hypochlorite.

5. The method of claim 4 wherein said inorganic hypochlorite salt is calcium hypochlorite.

6. The method of claim 4 wherein said inorganic salt of a hydroxy carboxylic acid is an inorganic salt of citric acid.

7. The method of claim 3 wherein said inorganic salt of a hydroxy carboxylic acid is an inorganic salt of citric acid.

8. The method of claim 7 wherein said inorganic salt of a hydroxy carboxylic acid is sodium citrate.

9. The method of claim 8 wherein said acid to adjust the pH to 4.5–8 is NaH_2PO_4.

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