

## UNITED STATES PATENT OFFICE

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## BLEACHING AND DISINFECTING AGENTS

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The present invention relates to improved bleaching and disinfecting agents.

Extensive research work has already been carried out on sodium chlorite and chlorine dioxide and on the application of these substances as bleaching agents, disinfectants or for other technical purposes. In practice, however, the use of these products, especially in aqueous solution and above all in acid aqueous solution, entails considerable difficulties owing to the strong corroding action of sodium chlorite and chlorine dioxide. Even when working in apparatus made of stainless steel, for instance iron-chrome-nickel alloys or iron-chrome-molybdenum alloys, or when using fixtures or goods carriers, such as tubes (spools) for cheeses (cross wound bobbins), warp beams or the like, made of stainless steel and mounted in apparatus of indifferent ceramic material, a heavy attack by the chlorites is observed. Especially in bleaching operations, however, should corrosion be strictly avoided, since it may give rise to discoloration of the goods to be bleached and to decomposition of the sodium chlorite or chlorine dioxide by catalytic action.

Various methods have been proposed to avoid corrosion in working with chlorine dioxide and chlorites. For instance, as is usual in other cases, the steel has been submitted to a passivation treatment before the introduction of chlorite solution, or sodium pyrophosphate has been added to the bleaching baths. The methods hitherto applied, however, have not completely overcome the difficulties indicated above and many textile factories have had to desist from the use of sodium chlorite and to apply less corrosive bleaching agents.

One feature of the present invention is based on the observation that the corrosion of stainless steel material in technical operations where-in chlorine dioxide or chlorite solutions are involved, particularly in bleaching processes, may be avoided by adding to the bleaching baths acids derived from nitrogen oxides and/or salts thereof.

According to this feature of the invention therefore in an industrial process carried out in apparatus consisting wholly or partly of stainless steel, especially a process of bleaching cellulosic and/or other material, a method is employed using as an active reagent a water-soluble chlorite or chlorine dioxide, in an aqueous solution containing in addition an acid derived from a nitrogen oxide and/or a salt of such an acid. Particularly useful is nitric acid or nitrates, especially sodium nitrate; furthermore, nitrous acid or its salts may be used since they are ox-

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dized with formation of nitric acid or nitrates and thereby become effective.

The acids and salts to be used according to this invention may be added to the bleaching baths in addition to the usual auxiliary agents necessary for adjusting the pH-value such as hydrochloric acid, acetic acid, phosphoric acid, bisulfates, primary ortho-phosphates or the like, either before or after the adjustment of the pH. It is also possible, however, to make use of the acids of the nitrogen oxides and the salts thereof for standardizing the pH necessary for the desired rate of bleaching.

The quantities, for instance, of nitrates to be added to the chlorite baths as a means for preventing corrosion, may vary within wide limits. Particularly in the case of low concentrations of  $\text{ClO}_2$ -ions or chlorine dioxide care must be taken, however, that the quantity of the nitrates added is not too small. It has been found that the quantities of the acids of nitrogen oxides required depend in each case on the percentage of  $\text{ClO}_2$ -ions or chlorine dioxide present in the bleaching solution, especially in the case of low concentrations. For instance, for 0.25 gram per liter of sodium chlorite (100%) about 0.23 gram per liter of sodium nitrate is required for obtaining sufficient protection against corrosion; this quantity suffices even in the case of low pH-values adjusted by means of corrosive acids (such as hydrochloric acid or sulfuric acid). For about 0.5 gram per liter of sodium chlorite (100%) about 0.46 gram per liter of sodium nitrate is required for preventing corrosion, particularly under unfavorable conditions. Satisfactory results under practically all conditions are obtained by using bleaching baths in which the radical of chlorous acid or chlorine dioxide and the radical of the acid derived from a nitrogen oxide, preferably nitric acid, are present in the molecular proportion of about 1:1. With concentrations of 1 gram or more of sodium chlorite per liter, in some cases, somewhat smaller quantities, for instance of nitrates, may be used without fear of corrosion. With such higher concentrations a molecular proportion of 1:0.6 may be sufficient.

According to a further feature of the invention an enhanced protection against corrosion is obtained by adding to the bleaching bath, besides the acid derived from a nitrogen oxide and/or a salt thereof, a sulfonic acid and/or carboxylic acid or a salt of either which acid or salt contains an aliphatic radical of high molecular weight which is interrupted by a carboxylic amide

or carboxylic ester group. The aliphatic radical should contain at least 6 carbon atoms.

As sulfonic acids or carboxylic acids of high molecular weight there enter into consideration, for instance, the reaction products of fatty acids with aminosulfonic acids or aminocarboxylic acids or with degraded proteins, furthermore condensation products from fatty acid salts and halogen carboxylic acids or halogen sulfonic acids. Special mention may be made of: oleyl-  
taurine, oleylmethylamine-acetic acid, stearoxy-  
methane sulfonic acid and stearoxyethane  
sulfonic acid. Such compounds are widely  
known as surface-active substances.

The pH of the bleaching baths may be adjusted by means of the usual inorganic and/or organic acids or salts thereof. The bleaching baths may also contain buffer substances such as sodium acetate, mono-phosphate, diphosphate or pyrophosphate, or the like.

Even a small addition of a specified carboxylic acid or sulfonic acid of high molecular weight will noticeably enhance the protection against corrosion. It is thus possible to avoid the minor corrosions which, due to the action over long periods of strongly acid baths (pH<2.8) or on account of too small additions of acids derived from nitrogen oxides, would, in the course of time, bring about a certain destructive effect upon the material used.

Moreover, the addition of a carboxylic acid or sulfonic acid of high molecular weight effects a good stabilization of the bleaching baths.

Since the decomposition of a sodium chlorite bath is accompanied by the escape of chlorine dioxide, the method of working according to the present invention results in far less inconvenience owing to the odor of chlorine dioxide. Fibrous material treated as described above is distinguished by a very good absorbing capacity.

The following examples serve to illustrate the invention but they are not intended to limit it thereto:

#### EXAMPLE 1

This example shows how corrosion may be prevented by the addition of nitric acid or a nitrate to a sodium chlorite bath.

Cheese spools wound with cellulosic yarn and made of stainless steel, marketed under the designation V4A, which spools each had a surface area of about 251 cm.<sup>2</sup>, were placed for 10 hours in a solution of 1.25 grams per liter of sodium chlorite having a pH=3 and at a temperature of 60° C. The pH was adjusted in separate cases:

- (a) With hydrochloric acid
- (b) With acetic acid
- (c) With nitric acid
- (d) With hydrochloric acid+0.5 gram of ammonium nitrate per liter.

Decrease of weight by corrosion:

- (a) 0.1072 gram: the yarn wound on the cheese was very heavily rust-stained
- (b) 0.0402 gram: the yarn wound on the cheese was heavily rust-stained
- (c) 0 gram: the yarn wound on the cheese was unstained
- (d) 0.0001 gram: the yarn wound on the cheese was unstained.

It is clear from the above that bleaching methods for cellulosic material based on either of experiments (c) and (d) will give satisfactory results.

#### EXAMPLE 2

This example shows how corrosion may be prevented and how sodium chlorite bleaching baths may be stabilized by the addition of a nitrate and a surface-active carboxylic acid or sulfonic acid.

Sheets of an iron alloy containing 0.1% C+18% Cr+10% Ni with additions of Mo and Ti were placed at 60-65° C. for 240 hours in baths containing 1 gram of sodium chlorite per liter and having a pH=3, the baths being renewed 10 times within the specified period. The pH-value was adjusted by means of hydrochloric acid. The decrease in weight by corrosion, calculated on 1 square decimeter, amounted to:

	Grams
(a) Without addition	0.6400
(b) +0.6 gram per liter of NaNO <sub>3</sub>	0.0040
(c) +0.6 gram per liter of NaNO <sub>3</sub> +0.25 gram per liter of oleylmethyltaurine	0.0012
(d) +0.6 gram per liter of NaNO <sub>3</sub> +0.3 gram per liter of a product obtained by condensation of a fatty acid with a degraded protein	0.0014
(e) +0.6 gram per liter of NaNO <sub>3</sub> +0.3 gram per liter of oleyl sarcoside	0.0016

Baths containing 1 gram of sodium chlorite per liter and having a pH=3 were prepared and the decrease, in percent, of the sodium chlorite content at 60° C. was determined after different periods of time.

#### Decrease in percent

	after 1½ hours	after 3 hours	after 18 hours
	Percent	Percent	Percent
(a) without addition	50	67	90
(b) with addition of 0.6 gram per liter of NaNO <sub>3</sub>	50	64	82
(c) with addition of 0.6 gram per liter of NaNO <sub>3</sub> +0.25 gram per liter of oleylmethyltaurine	11	23	49
(d) with addition of 0.6 gram per liter of NaNO <sub>3</sub> +0.3 gram per liter of a product obtained by condensation of a fatty acid and a degraded protein	29	35	58
(e) with addition of 0.6 gram per liter of NaNO <sub>3</sub> +0.3 gram per liter of oleyl sarcoside	31	50	58

#### I claim:

1. A method of inhibiting the corrosion of stainless steel in contact with an acidic aqueous solution of a water-soluble chlorite comprising: adding to said solution an alkali metal nitrate in an amount ranging from about .6 mole to about 1.0 mole for each mole of the water-soluble chlorite.

2. A method according to claim 1, comprising the further addition of a member selected from the group consisting of sulfonic acids and carboxylic acids containing an aliphatic radical of high molecular weight which is interrupted by a carboxylic amide group and of the sulfonic acids and carboxylic acids containing an aliphatic radical of high molecular weight which is interrupted by a carboxylic ester group and of the salts thereof.

3. A method of inhibiting the corrosion of stainless steel in contact with an acidic aqueous solution of a water-soluble chlorite comprising: adding to said solution sodium nitrate in an amount ranging from about .6 mole to about 1.0 mole for each mole of water-soluble chlorite and further adding the sodium salt of a sulfonic acid containing an aliphatic radical of high molec-

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ular weight which is interrupted by a carboxylic amide group.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,071,091	Taylor -----	Feb. 16, 1937
2,260,367	Du Beau et al. -----	Oct. 28, 1941
2,477,631	Levy -----	Aug. 2, 1949

Number  
552,711

6  
FOREIGN PATENTS

Country	Date
Great Britain -----	Apr. 21, 1943

OTHER REFERENCES

Mellor: "Modern Inorganic Chemistry," 1944, p. 512; Longmans, Green and Co. (Copy in Div. 64.)