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3,749,672

## STABILIZED SOLUTIONS OF N-HALO COMPOUNDS

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No Drawing. Continuation-in-part of application Ser. No. 6,540, Jan. 28, 1970, which is a continuation-in-part of application Ser. No. 768,165, Oct. 16, 1968, which in turn is a continuation-in-part of application Ser. No. 729,461, May 15, 1968, all now abandoned. This application Apr. 19, 1971, Ser. No. 135,373

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12 Claims

### ABSTRACT OF THE DISCLOSURE

Described and claimed are stable aqueous systems containing an N-hydrogen compound and a hypobromite, hypochlorite or hypoiodite in equilibrium with the corresponding N-halo compound or compounds. Stability is provided by inclusion of a buffer which maintains pH of the system between 4 and 11. The systems can be used wherever gradual release of active halogen is desired, e.g. as household laundry or industrial bleaches or as agents for control of micro-organisms in process water streams.

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 6,540, filed Jan. 28, 1970, now abandoned, which is a continuation-in-part of Ser. No. 768,165, filed Oct. 16, 1968, now abandoned, which is in turn a continuation-in-part of Ser. No. 729,461, filed May 15, 1968, and now abandoned. In the first two applications, the stabilized solutions of this invention were described with reference to their use as household laundry bleaches. In this continuing application and the application immediately preceding there are described other uses for the solutions, especially the use in controlling micro-organisms.

### BACKGROUND OF THE INVENTION

Bleaching agents are divided into two basic classes: oxidizing bleaches and reducing bleaches. Reducing bleaches, such as bisulfite-containing compositions, are primarily used in the textile industry. On the other hand, oxidizing bleaches, which contain compounds such as chlorine, low oxyacids of chlorine, N-chloro compounds and compounds containing a peroxy linkage, are commonly used as household laundry bleaches and in paper pulp bleaching. The most widely used oxidizing bleaches for household laundry applications are the hypochlorite and oxygen bleaches. Hypochlorite bleaches normally contain 5 to 6 percent by weight aqueous solutions of sodium hypochlorite. Oxygen bleaches, sometimes called the safe bleaches, contain persulfate or perborate compounds such as potassium mono-persulfate and sodium perborate. Although hypochlorite bleaches have a better bleaching capability than oxygen bleaches, the use of hypochlorite bleaches often results in fabric damage and excessive dye removal. It is known, for example, that strong hypochlorite bleaches have a harmful effect on textiles and textile-treating resins made from synthetic polymers which contain a significant portion of NH groups in the resin molecule. Examples of such polymers

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are: melamine-formaldehyde resins, open-chain urea-formaldehyde resins and cyclic urea-formaldehyde resins. After a number of washings, fabrics made from such synthetic polymers acquire a yellowish color and often decompose when exposed to high temperatures. Non-synthetic fabrics, such as wool and silk are also yellowed when treated with strong hypochlorite bleaches.

In addition, hypochlorite bleaches exhibit a more rapid decomposition upon storage and are, therefore, less stable than oxygen bleaches. In contrast, oxygen bleaches do not have the high bleaching ability of hypochlorite bleaches, but their use in household laundry applications results in less dye removal from the fabric and less fabric damage.

The deficiencies of the prior art bleaching compositions make it desirable to produce a bleaching composition which has a bleaching ability approaching that of the strong hypochlorite bleaches but which is as safe for dyes and fabrics as the oxygen bleaches.

Although bleaching compositions containing aqueous solutions of a hypochlorite, an N-hydrogen compound and the corresponding N-chloro compound or compounds, are known in the prior art, such compositions are designed for immediate use as a bleach because of their inherent instability and rapid loss of bleaching activity. Solid N-chloro compounds, for example, are sold and used as bleaching compositions and are designed for such immediate use because of their relative instability in solution.

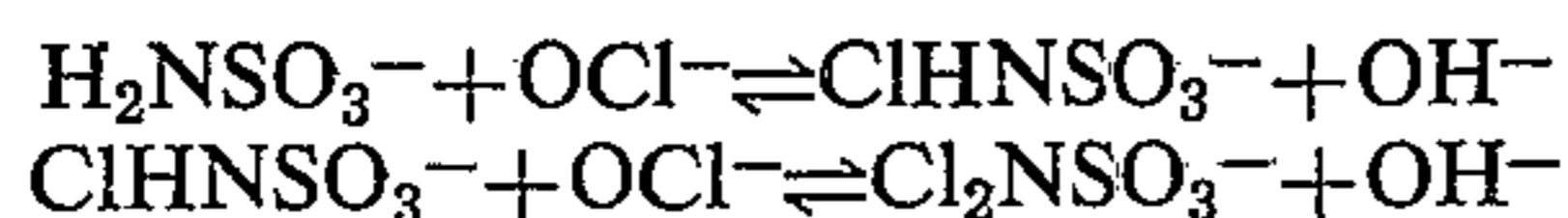
N-chloro compounds have also been used heretofore to control the growth of micro-organisms in process water streams. U.S. Pat. 3,328,294, issued June 27, 1967, describes the use of N-monochlorosulfamic acid and N,N-dichlorosulfamic acid and their alkali and alkaline earth metal salts for this purpose, especially in papermaking. When placed in the process stream at very low concentration, the N-chlorosulfamic acid slowly releases hypochlorite. However, as described in column 5, lines 21 to 31 of the patent, in concentrated solution the N-chlorosulfamic acid decomposes relatively rapidly. The N-chlorosulfamic acid must, therefore, be used within a short time after it is prepared. It is not suitable for preparation and subsequent storage without great loss of active chlorine. This loss prevents long transportation and storage which are necessary for a commercial product.

### SUMMARY OF THE INVENTION

According to this invention, there are provided aqueous systems which contain an N-hydrogen compound and a hypobromite, hypochlorite or hypoiodite, in equilibrium with the corresponding N-halo compound or compounds, the N-halo compounds being present in a concentration of  $1 \times 10^{-3}$  to 1.0 molar. The systems have improved stability due to control of the stoichiometry and inclusion of a buffer, the mole ratio of buffer to N-halo compound being at least 1:10, which maintains the pH in a stable range between 4 and 11. The invention also provides a method of making the above aqueous systems, in which the N-halo compounds are N-bromo or N-chloro compounds, which comprises mixing the N-hydrogen compound with a hypobromite or hypochlorite in the presence of water and a buffer which maintains the pH in a stable range between 4 and 11. The systems containing hypoiodite and N-iodo compounds in equilibrium with N-hydrogen compounds are made by reacting the elemental iodine with the N-hydrogen compound in water in presence of an alkali and a buffer.

The invention can be best explained by referring to a specific embodiment, e.g. an aqueous solution of N,N-di-

chlorosulfamate. The equilibrium equations for this system are as follows:

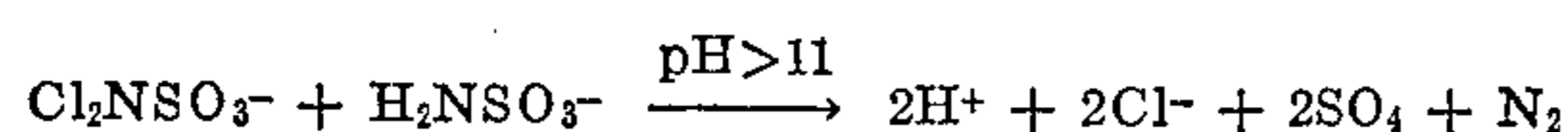


The equilibrium of this system favors the formation of N,N-dichlorosulfamate ion, so the concentration of free hypochlorite, i.e. hypochlorite present in solution at equilibrium conditions, is maintained at a low level. However, as the free hypochlorite is depleted during use of the solution, more hypochlorite is produced, owing to the tendency of the system to return to equilibrium. Thus, the solution can be used where it is desired to have a controlled availability of hypochlorite ion, e.g. as a household laundry bleach or as an additive to process water streams for controlling growth of micro-organisms.

In the former use, due to the fact that there is a small amount of hypochlorite present, the system may safely be used to bleach dyed fabrics without adversely affecting the fabric or the dye. In the latter case, the slow release of hypochlorite minimizes undesirable side reactions, such as the corrosion of the process equipment and attack on materials other than the micro-organisms.

Dichlorosulfamates decompose under highly alkaline conditions (pH > 11), forming nitrogen gas, sulfate, and chloride, and under acid conditions, by hydrolysis, to chloramines and sulfuric acid. In either case, decomposition causes the system to become more acid. This decomposition is relatively slow at pH's between 4 and 11, but under extreme acid or alkaline conditions, the decomposition becomes rapid. Heretofore, compositions of N,N-dichlorosulfamates have not been synthesized in high yield (>90%) since, in the prior art syntheses, the pH was allowed to stray outside these limits. Furthermore, once made, the dichlorosulfamate decomposed rapidly, especially when the inevitable acidic conditions occurred on standing.

The purpose of the buffer is to establish and maintain a pH between 4 and 11 in order to prevent rapid decomposition. Thus, during preparation of the N-chlorosulfamate, the buffer takes up the alkali produced, and prevents the pH from exceeding 11. The equations above show that the preparation of monohalo and dihalo nitrogen compounds of this invention is accompanied by the production of basic hydroxide ion. This is illustrated by the reaction of hypochlorite with sulfamic acid (a typical N—H compound of this invention). Thus the pH of the solution rises rapidly during the preparation of the N-halo compound, and will rise above 11, a point at which decomposition becomes rapid, if a buffer is not included.



Heretofore, this was not recognized in the art because prior art dealt with very dilute solutions wherein the preponderance of solvent prevented an excessive rise in pH. However, for solutions which contain the N—H compound in concentrations of greater than  $1 \times 10^{-3}$  molar the liberated hydroxide will be sufficient to cause a pH of 11 to be exceeded. Therefore, the inclusion of a buffer to neutralize the by-product  $\text{OH}^-$  is mandatory for good yields.

But equally important is the need for the buffer in the composition after it is made. The buffer serves to neutralize acid ( $\text{H}^+$ ) produced on storage and thus increases the stability of the N-halo compound. It is important from a commercial standpoint to have good stability. The product must be transported and then stored by the customer. As will be appreciated, the user wants as much active chlorine as possible and poor stability defeats his economic considerations.

A further purpose of the buffer is to establish and maintain the pH at a level which will provide the desired amount of hypochlorite in the system. As shown by the

above equilibrium equations for the hypochlorite-sulfamate system, free hypochlorite increases with increasing hydroxyl ion concentration. For this reason, the preferred solutions are those which are buffered to a pH in the range of 7 to 11.

When used as a bleaching composition the N,N-dichlorosulfamate solutions provide a unique balance between a bleaching ability which approaches that of strong hypochlorite bleaches, and fabric and dye safety which approximates the safety of oxygen bleaches. In addition, the solutions exhibit improved stability as compared to sodium hypochlorite solutions.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

As used in this invention the term N-hydrogen compound means a Bronsted acid amide which contains at least 1 N—H bond. That is, N-hydrogen compounds are those having an N—H or  $\text{NH}_2$  group adjacent to an electron withdrawing functional group such as  $\text{C}=\text{O}$ ,  $\text{S}=\text{O}$  or  $\text{P}=\text{O}$ . In this invention N-hydrogen compounds are limited to those having a dissociation constant ( $\text{pK}_b$ ) greater than 5 with the proviso that the conjugate base of the Bronsted acid is not halogen or halogen oxide. Examples are below:

Acid	Acid amide derivative
Hydrogen cyanide.....	Cyanamide, dicyandiamide, melamine.
Carbonic acid.....	Ethyl carbamate, urea, thiourea, 1,3-dimethylbiuret, methyl phenylbiuret, isocyanuric acid, barbituric acid, 6-methyluracil, uron, 2-imidazolinone, ethylene urea, 5,5-dimethylhydantoin, 2-pyrimidinone.
Carboxylic acids.....	Benzamide, phthalimide, N-ethylacetamide.
Amino acids.....	Azetid-2-one, 2-pyrrolidone, caprolactam.
Sulfuric acid.....	Sulfamic acid, sulfamide, p-toluenesulfonamide, phenyl sulfinamide, phenyl sulfinimidylamide, diphenyl sulfonimide, dimethyl sulfinimine, isothiazolene-1,1-dioxide.
Phosphoric acid.....	Orthophosphoryl triamide, pyrophosphoryl triamide, phenyl phosphoryl-bis dimethylamide.
Boric acid.....	Boric acid amide.

The hypochlorite or hypobromite is preferably sodium, potassium, calcium, or magnesium hypochlorite or hypobromite. When the solution is made by the elemental halogen/alkali route, the alkali is preferably sodium or potassium hydroxide.

As used in this invention the term buffer is defined as a weak acid ( $\text{pK}_a=4-13$ ) and its conjugate base (alkali metal or alkaline earth metal salt of the weak acid). These would be exemplified as acetic acid and acetate salts, boric acid and borate salts, arsenous acid and arsenate salts, carbonic acid and carbonate salts, phosphoric acids and phosphate salts, and silicic acids and silicate salts. The particular buffer or combination of buffers will depend upon the pH desired and the solubility requirements. The amount of buffer used should exceed 10 mole percent of the N-halo compound in the system.

This invention is based upon the discovery that buffered aqueous solutions obtained by adding a hypochlorite, such as sodium hypochlorite, to certain N-hydrogen compounds, such as sulfamic acid, are highly desirable as bleaching compositions. Bleaching compositions of the invention contain an amount of buffer sufficient to maintain a free hypochlorite concentration between  $0.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  moles per liter of laundry solution when the bleach is diluted with water to normal laundry concentration, e.g.  $10^{-3}$  molar, or 500-1000 fold. In a typical laundry application, the bleaching compositions are diluted to a level of 30 parts per million of active oxygen.

Using equilibrium data for the hypochlorite-sulfamate system described above, it is possible to determine the concentration of free hypochlorite at various laundry conditions. Table I shows the results of such a determination.

TABLE I.—TOTAL AND FREE HYPOCHLORITE CONCENTRATIONS FOR DICHLOROSULFAMATE

Bleaching compositions		
pH	Total available hypochlorite moles [OCl <sup>-</sup> ]/liter of solution	Free hypochlorite moles [OCl <sup>-</sup> ]/liter of solution
8	0.1	1.2×10 <sup>-4</sup>
9	0.001	1.0×10 <sup>-4</sup>
9	0.002	1.5×10 <sup>-4</sup>
9	0.1	6.9×10 <sup>-4</sup>
10	0.001	2.3×10 <sup>-4</sup>
10	0.002	3.1×10 <sup>-4</sup>
10	0.1	1.2×10 <sup>-3</sup>

As the pH of the laundry solution is increased, the concentration of free hypochlorite increases with the resultant expected increase in the bleaching ability of the hypochlorite-sulfamate system. In contrast, a conventional hypochlorite bleaching composition contains approximately 10<sup>-3</sup> moles of free hypochlorite per liter of laundry solution under similar dilutions.

Although aqueous hypochlorite-sulfamate systems and other solutions of N-halo compounds are known to be unstable, this invention provides bleaching compositions which are at least as stable as sodium hypochlorite solutions at similar concentrations. The improved stability of the bleaching compositions of this invention is obtained through careful control of the stoichiometry of the system at various pH's and through the addition of suitable buffers to the system. At N-halo concentrations of 1×10<sup>-3</sup> to 1.0 molar, the inclusion of a buffer as taught by this invention is mandatory for good yield and stability of the N-halo compound.

Table II illustrates the effect controlling the mole ratio of hypochlorite to sulfamic acid has on bleach stability at neutral pH (pH=7.0), for example, reported in terms of loss of active chlorine (expressed as "percent active oxygen," which is defined as the equivalents of iodine released from potassium iodide, per gram of sample, multiplied by 0.1 times the equivalent weight of oxygen).

TABLE II

Effect of mole ratio on bleach stability at neutral pH

Mole ratio (NaOCl/HSO <sub>3</sub> NH <sub>2</sub> ):	Percent of initial A.O. after 12 days
1.75	88.5
2.00	92.5
2.25	82.5
2.50	68.5
2.75	57.5
3.00	37.5

While maximum stability of the bleaching compositions is achieved by maintaining a 2:1 hypochlorite to sulfamate mole ratio at neutral pH, maximum bleach stability is accomplished under basic conditions by maintaining an excess of hypochlorite (e.g., mole ratio greater than 2:1). Under acid conditions, however, the bleaching compositions are found to be most stable when there is an excess of sulfamate (e.g., mole ratio less than 2:1). Typically, in the sense of this invention, acid conditions refer to a pH range of about 4.0 to 6.9 while basic conditions refer to a pH range of about 7.1 to 11.

The effect of pH and mole ratio on bleach stability is shown in Tables III and IV.

TABLE III

Effect of mole ratio on bleach stability at pH=5

Mole ratio (NaOCl/HSO <sub>3</sub> NH <sub>2</sub> ):	Percent of initial A.O. after 2 weeks
1.5	97.5
1.7	97.5
2.0	97.5
2.1 or more	10

<sup>1</sup> Decomposition in several hours.

TABLE IV

Effect of mole ratio on bleach stability at pH=9.5

Mole ratio (NaOCl/HSO <sub>3</sub> NH <sub>2</sub> ):	Percent of initial A.O. after 2 weeks
1.5	38.0
1.7	82.0
2.0	89.0
2.3	92.2
2.5	93.5

Under basic conditions the preferred range of suitable mole ratios of hypochlorite to sulfamate is about 2.05 to 3.0, since the decomposition rate of the bleach compositions begins to increase at mole ratios greater than 3.0.

While stable bleaching compositions are often made at normal concentration levels, it is also possible to prepare more concentrated bleaching compositions by reducing the amount of water used in the bleach formulations. For example, bleaching compositions having approximately twice the active oxygen level of normal hypochlorite bleaches are shown to possess similar stability characteristics. The use these doubly concentrated bleaching compositions, of course, would reduce the amount of bleach required on a per wash basis.

The preferred mole ratio of hypochlorite to N-hydrogen compound varies depending on the N-hydrogen compound used. Table V illustrates the preferred mole ratios of hypochlorite to N-hydrogen compound necessary to produce bleaching compositions having maximum stability at neutral pH.

TABLE V

Mole ratio of hypochlorite to N-hydrogen compound

Amine:	Mole ratio
Sulfamic acid	2
Sulfamide	4
Trisulfimide	3
Para-toluenesulfonamide	2
Melamine	6
Sodium trimidometaphosphate	3
5,5 - dimethylhydantoin	2

As one would expect, the mole ratio also affects the bleaching ability and dye removal capability of the system. Bleaching ability, as measured by the difference in reflectance of a stained cloth before and after washing with bleach and detergent, and dye removal, e.g., observing the effect of concentrated bleach on a dyed textile fabric, are appreciably affected by the mole ratio of hypochlorite to N-hydrogen compound. In the hypochlorite-sulfamic acid system, as the mole ratio of sodium hypochlorite/sulfamic acid is increased above 2/1 a gradual increase in bleaching ability that approaches bleaching accomplished with 5% solutions of sodium hypochlorite results. As the ratio is increased above 2/1 dye removal is also increased. At ratios less than 2/1 both bleaching ability and dye removal are reduced.

Typical formulations of this invention in which sulfamic acid is used as the N-hydrogen component are shown in Table VI.

TABLE VI

	Wt. percent	Moles/kg.
EXAMPLE I—PHOSPHATE-BUFFERED COMPOSITION		
Water	42.5	
Sulfamic acid	3.5	.36
Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	5.9	
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	5.1	
Sodium hypochlorite (2.75% A.O.)	42.0	.72
EXAMPLE II—BORAX-BUFFERED COMPOSITION		
Water	37.0	
Sulfamic acid	4.0	.41
Borax	10.0	
Sodium hypochlorite (2.74% A.O.)	49.0	.82

TABLE VI—Continued

	Wt. percent	Moles/kg.
<b>EXAMPLE III—SODIUM CARBONATE-ACETATE BUFFERED COMPOSITION</b>		
Water.....	42.86	.....
Sulfamic acid.....	3.88	.40
Acetic acid.....	2.12	.35
Sodium hypochlorite (2.74% A.O.).....	46.62	.80
Sodium sesquicarbonate.....	4.52	1.40
<b>EXAMPLE IV—POTASSIUM CARBONATE-BUFFERED COMPOSITION</b>		
Water.....	49.5	.....
Sulfamic acid.....	3.5	.36
Acetic acid.....	2.1	.35
Sodium hypochlorite (3.20% A.O.).....	37.3	.72
Potassium carbonate.....	1.5	.11
Potassium bicarbonate.....	6.1	.61
<b>EXAMPLE V—BICARBONATE-BUFFERED COMPOSITION, 0.4 MOLAL</b>		
Sulfamic acid.....	3.88	.40
Water.....	38.3	.....
25% w./w. sodium hydroxide.....	6.4	.40
Sodium bicarbonate.....	6.72	.80
Sodium hypochlorite (2.87% A.O.).....	44.69	.80
<b>EXAMPLE VI—BICARBONATE-BUFFERED COMPOSITION, 0.55 MOLAL</b>		
Sulfamic acid.....	5.34	.57
Water.....	15.17	.....
25% w./w. sodium hydroxide.....	8.80	.55
Sodium bicarbonate.....	9.24	1.10
Sodium hypochlorite (2.87% A.O.).....	61.45	1.10
<b>EXAMPLE VII—BICARBONATE-BUFFERED COMPOSITION</b>		
Sulfamic acid.....	3.25	.33
Water.....	42.72	.....
50% w./w. sodium hydroxide.....	2.65	.33
Sodium bicarbonate.....	5.64	.67
Sodium hypochlorite (2.80% A.O.).....	45.74	.80
<b>EXAMPLE VIII—BICARBONATE-BUFFERED COMPOSITION, 0.70 MOLAL</b>		
Sulfamic acid.....	6.80	0.70
Water.....	5.04	.....
Sodium hypochlorite (2.80% A.O.).....	82.28	1.44
Sodium bicarbonate.....	5.88	0.70

<sup>1</sup> Calculated as carbonate.

To obtain other compositions of this invention, one can substitute sulfamide, trisulfimide, para-toluene-sulfonamide, melamine, 5,5-dimethylhydantoin, sodium trimidometaphosphate and other N-hydrogen compounds for sulfamic acid in the above formulations.

In order to compare the bleaching efficiency and safety of the bleaching compositions of this invention with strong hypochlorite and oxygen bleaches, the percent whiteness for various prestained cloths relative to unstained cloths was measured after washing at 158° F. for 20 min. The results are shown in Table VII.

TABLE VII

Wash system	Free hypochlorite (moles/ liter of solution)	Whiteness index (percent whiteness)
<b>I.—COFFEE-TEA STAIN REMOVAL FROM COTTON CLOTH</b>		
5% solution of sodium hypochlorite and detergent.....	2×10 <sup>-3</sup>	85.1
Bleaching Composition I in Table VI and detergent.....	1.5×10 <sup>-4</sup>	83.6
Bleaching Composition II in Table VI and detergent.....	1.5×10 <sup>-4</sup>	80.8
Granular bleach containing potassium monopersulfate and detergent.....	0	62.8
Detergent only.....	0	58.8
<b>II.—DYE REMOVAL FROM DYED COTTON CLOTH</b>		
No washing.....	.....	12.5
Detergent only.....	0	12.5
Granular bleach containing potassium monopersulfate and detergent.....	0	13.8
Bleaching Composition I in Table VI and detergent.....	1.5×10 <sup>-4</sup>	14.1
Bleaching Composition II in Table VI and detergent.....	1.5×10 <sup>-4</sup>	14.8
5% solution of sodium hypochlorite and detergent.....	2×10 <sup>-3</sup>	23.8

Although the invention can best be illustrated with sulfamic acid, it is understood that the procedures described below can be used equally well with other compounds having at least one NH or NH<sub>2</sub> group which can react with hypochlorite to form an NX, NHX or NX<sub>2</sub> group.

The N,N-dichlorosulfamate bleaching systems of this invention can be prepared by several processes. In the process described herein, a sulfamic acid solution is reacted with sodium hypochlorite in the presence of a buffer. Normally, buffer salts such as sodium phosphate, are added to an aqueous sulfamic acid solution before sodium hypochlorite is mixed with the solution. In some cases, however, a buffering agent such as acetic acid, is first mixed with the aqueous sulfamic acid solution before sodium hypochlorite and additional buffer salts, such as potassium carbonate, are mixed with the acid solution.

The buffer absorbs the alkalinity generated by the hypochlorite-sulfamic acid reaction and thereby reduces the possibility of decomposition of the N,N-dichlorosulfamate at pH ranges of 11 or higher to nitrogen gas, sulfate and chloride. In addition, the presence of a buffer in the bleaching composition improves the stability of the N,N-dichlorosulfamate by resisting the generation of the acid condition (e.g., pH less than 6) associated with decomposition of N,N-dichlorosulfamate.

If phosphate buffers are used, the phosphate salts and sulfamic acid are first dissolved in water. Then the sodium hypochlorite is mixed with the acid-buffer solution. When carbonate buffers are used in the bleaching composition, often a sulfamic acid-acetic acid solution is first prepared by dissolving sulfamic acid and acetic acid in water. Then the sulfamic acid in solution with acetic acid is reacted with sodium hypochlorite. Finally, the carbonate buffer is added as either a solid carbonate salt or in solution by reducing the amount of water in the reaction mixture. The carbonated buffer is added after the sulfamic acid-hypochlorite reaction occurs because the carbonate buffer may decompose in an acid medium.

The other N-halo compounds of this invention are prepared by methods similar to those described above.

The following examples illustrate the preparation of bleaching compositions of this invention. All parts and percentages are by weight unless otherwise specified.

#### Example 1

A solution of an N,N-dichlorosulfamate bleaching composition is made by mixing and dissolving 507.3 parts water, 35.0 parts sulfamic acid, 34.8 parts tripotassium phosphate, and 50.3 parts monopotassium phosphate in an insulated 1000 ml. glass vessel equipped with a "Teflon" agitator and thermometer. Next 372.6 parts of a 14% by weight sodium hypochlorite solution with 3.1% active oxygen is rapidly added to the beaker while the sulfamic acid-phosphate solution is agitated. A bleach composition having 1.15% active oxygen and a pH of 10.6 is produced by this procedure. A temperature rise of approximately 15° C. results during the sulfamic acid-hypochlorite reaction, but no noticeable effect on bleach stability results when reaction temperatures are varied from 10° C. to 50° C. After three months of storage the bleaching composition prepared by this procedure has 0.96% active oxygen at a pH of 7.9.

#### Example 2

The procedure of Example 1 is repeated except that the buffer salts, tripotassium phosphate and monopotassium phosphate are replaced by potassium hydroxide and phosphoric acid. No significant differences are found in the bleaching composition properties. The initial percent active oxygen of the bleach was 1.16 and the pH was 10.3. After three months the percent active oxygen was 0.96 and the pH was 8.3.

## Example 3

The procedure of Example 1 is repeated except that 160 parts phosphoric acid are substituted for the buffer salts, tripotassium phosphate and monopotassium phosphate. The addition of phosphoric acid increases the acidity of the system and generates sufficient buffer in situ ( $\text{Na}^+$  from hypochlorite) to limit the change in pH upon hypochlorite addition. The initial percent active oxygen of the resulting bleaching composition is 1.10 at a pH of 10.5. After storage for three months, the bleaching composition had 0.98% active oxygen and a pH of 7.5.

## Example 4

An N,N-dichlorosulfamate bleaching composition is prepared by first mixing and dissolving 35.0 parts sulfamic acid and 21.0 parts acetic acid with 494.9 parts water in a 20 gallon polyethylene lined drum equipped with an air motor driven unplasticized poly(vinyl chloride) agitator and glass thermometer. The 372.6 parts of a 14% by weight sodium hypochlorite solution having a 3.1% active oxygen is rapidly added to the drum while the sulfamic acid-acetic acid solution is agitated. Finally, 15.3 parts potassium carbonate and 61.2 parts potassium bicarbonate are added to the drum in solid form. The bleach formed from this procedure had 1.15% active oxygen and a pH of 8.8.

## Example 5

The procedure of Example 4 is followed except that 520.8 parts water is used instead of 494.9 parts, 21.7 parts acetic acid is used instead of 21.0 parts, and 49.9 parts sodium sesquicarbonate is used instead of 15.3 parts potassium carbonate and 61.2 parts potassium bicarbonate. The bleach formed from this procedure has 1.15% active oxygen and a pH of 9.5.

## Example 6

N,N-dichlorosulfamate bleach is prepared by adding 530.8 parts of a 14% sodium hypochlorite solution having 2.67% active oxygen to a 20 gallon polyethylene lined drum equipped with an air motor driven unplasticized polyvinyl chloride agitator and a glass thermometer. Next 462.6 parts of water, 35.0 parts sulfamic acid and 21.6 parts acetic acid are premixed in a separate container and then rapidly added to the sodium hypochlorite. Finally, 50.0 parts sodium sesquicarbonate is mixed and dissolved in the hypochlorite-sulfamic acid reaction mixture. The resultant bleach formed by this procedure has an active oxygen level of 1.15% and a pH of 9.2.

The process described in Examples 1-6 can also be adapted to a continuous process for making sulfamate bleach in which hypochlorite and sulfamic-acidic acid solutions are mixed on a continuous basis. In the continuous process, significant hold-up of partially reacted mixtures at low pH is reduced, and thus the possibility of chloramine formation is minimized. In addition, the commercial acceptability of the continuous process exceeds that of the batch process. The following example defines and illustrates the preparation of the bleaching compositions of this invention using a continuous process.

## Example 7

A sulfamic acid-acetic acid solution is prepared by mixing and dissolving 67.7 parts sulfamic acid, 41.7 parts acetic acid and 890.7 parts water. The acid mixture is then placed into a polyethylene lined drum equipped with a tubular outlet closed-off by an unplasticized poly(vinyl chloride) valve. A 14% by weight solution of sodium hypochlorite is placed into a similar drum. The two reaction streams (sulfamic-acetic acid solution and sodium hypochlorite solution) are then pumped by a 316 stainless steel duplex reciprocating metering pump into the side outlets of a mixing T. These streams are mixed and reacted as they discharge from the mixing T. The heat of reaction is absorbed by the reaction system and results in an adi-

abatic temperature rise during reaction. The reaction temperature however, varies from 30° C. to 40° C. The effluent is discharged into a 500 ml. large mouth flask for pH and temperature measurement and then overflows into a product receiver. Sufficient sodium sesquicarbonate is added to the produce receiver to make the weight percent of sodium sesquicarbonate based on total weight of product approximately 5%. Fluid velocity through the mixing T and 6 inches of ¼ inch of polyethylene tubing downstream of the T is approximately 10 feet/second. The flow rates of the acid and hypochlorite streams are adjusted to provide the mixing T with approximately 1.2 pounds of sulfamic acid-acetic acid solution per pound of sodium hypochlorite solution. During the course of the continuous run, samples of the effluent are taken at approximately 10 minute intervals.

## Example 8

A solution of a doubly concentrated N,N-dichlorosulfamate bleaching composition is made by first preparing a slurry of 5.88 parts sodium bicarbonate and 82.28 parts of sodium hypochlorite (having 2.80% active oxygen) in a class vessel. A second slurry is prepared having 5.04 parts water and 6.80 parts sulfamic acid. The water-sulfamic acid slurry is then added to the bicarbonate-hypochlorite slurry while the mixture is stirring. A temperature rise of 30° C. results during the sulfamic acid-hypochlorite reaction. The initial active oxygen level of the resultant bleaching composition is 2.1, at an initial pH of 9.5. This concentrate bleaching composition exhibits excellent stability characteristics upon storage.

The solutions of this invention can be used for other purposes besides household laundry bleach. The solutions of N-chloro and N-bromo compounds can be used in other bleaching applications, such as bleaching paper pulp. They can also be used to control micro-organisms in process water streams, e.g. in paper-making processes and waste-treatment plants, and as halogenating agents.

To eliminate slime causing bacteria or to prevent infestation of microorganisms which cause slime formation in pulp and paper mills, N-chlorosulfamates can be added to paper machine stock, to process streams of paper pulp stock, to white water systems or other recirculating water systems and to paper coatings containing organic adhesives such as starch, or casein which are subject to bacterial degradation. To eliminate slime from an infested stock or process system, the dosage of N-chlorosulfamate added will be such as to yield on the order of 3-10 p.p.m. of active chlorine in the water. When this level of active chlorine has been reached in all parts of the affected system, the microorganisms will rapidly be eliminated or reduced to a level at which slime formation will cease. Higher levels of active chlorine can thereafter be maintained, as for example 10 p.p.m., but such quantities are not ordinarily needed for control purposes. When the slime forming organisms have been eliminated and a clean system has been achieved, the level of active chlorine needed to maintain good control throughout the system can be on the order of 1-5 p.p.m. The system will remain essentially sterile under such conditions. The solutions of buffered N-iodo compounds are useful as sanitizers, e.g. for toilet bowls. The solutions may also be used as halogenation agents.

## Example 9

The N,N-dichlorosulfamate composition of Example 8 above is a preferred slimicide composition. This composition is added to the wet streams of a paper mill system which is highly infested with microorganisms. The infestation is apparent because of extensive growth of slime. After a few days the treatment is limited to addition at the major sources of contamination or effective control points, e.g. raw water, white water, stock feed to the paper machine, etc. The treatment prevents contamination of the entire mill system. Throughout the above

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treatment, the buffered N,N-dichlorosulfamate of Example 8 is added at a rate sufficient to maintain an active chlorine concentration of 1-5 parts per million parts of water. After two weeks from the beginning of the treatment, the system is essentially sterile, and remains so as long as the chlorinated sulfamate is added.

## Example 10

An aqueous solution containing 14.5% sodium hypochlorite is prepared by adding chlorine to sodium hydroxide solution. A solution of 27 parts of sulfamic acid in 200 parts of water is added to a solution made from 300 parts of 14.5% sodium hypochlorite solution, 36 parts of sodium bicarbonate, and 437 parts of water. The rate of addition is controlled so that the temperature rise is not excessive. The final solution is 0.26 molal in sodium N,N-dichlorosulfamate. The solution has a positive chlorine value of 4.23%. The pH is 10-10.5 and the percent solids is approximately 10%.

The following example demonstrates the result when the solution is not buffered.

## Example 11

Example 10 is repeated except that the sodium bicarbonate is not added. The final solution has an active chlorine value of only 3.15%. On standing, this solution loses its active chlorine content at a very rapid rate.

## Example 12

A suspension of 12.8 parts of barbituric acid in 70 parts of water is added to a solution of 100 parts 14.5% sodium hypochlorite plus 150 parts of water and 17 parts of sodium bicarbonate. The rate of addition is controlled so the temperature rise is not excessive. The final solution contains N,N'-dichlorobarbiturate in a buffer system of carbonate-bicarbonate.

The following table illustrates further examples for the prepared of the NX and NX<sub>2</sub> compounds of this invention. The examples are based upon Example 12 where the N-H compound is substituted for barbituric acid of Example 12.

Example:	N-H compound	No. of parts of N-H compound	Parts of 14.5% NaOCl solution
13	Sulfamide	9.6	212
14	p-Toluenesulfonamide	17.1	106
15	Methanesulfonamide	9.5	106
16	Melamine	12.6	318
17	2-imidazolinone	8.6	106
18	Pyrrolidone	8.5	53
19	5,5-dimethylhydantoin	11.4	106
20	Hydantoin	1.0	106
21	Acetanilide	13.5	53
22	N-ethylacetamide	8.7	53
23	Acetamide	5.9	53
24	Phthalimide	14.7	53
25	Benzamide	12.1	106
26	Cyanamide*	4.2	106
27	Urea	6.0	212
28	N-methylurea	7.4	159
29	Acetylurea	10.2	159
30	Biuret	12.1	265
31	Ethyl allophanate	13.2	159
32	Ethyl carbamate	8.9	106
33	Pyrrole	6.7	53
34	Indole	7.7	53

\*This compound must be chlorinated and stabilized at pH 4.5.

## Example 35

A suspension of 9.9 (0.10 mole) of succinimide and 200 parts of water is treated with 0.1 mole of sodium bicarbonate. This mixture is cooled to 0° C. and treated with 0.1 mole of cold aqueous solution hypobromite. The resulting product is N-bromosuccinimide stabilized by a carbonate-bicarbonate buffer system.

## Example 36

The N-chloro-N-ethylacetamide produced in Example 21 is treated with sodium iodide. The product is N-ethyl-N-iodoacetamide which is buffered by a bicarbonate-carbonate buffer system.

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## Example 37

To a stirred solution consisting of 400.0 g. of water, 30.0 g. of sodium hydroxide and 72.75 g. of sulfamic acid is added simultaneously 106.5 g. of chlorine gas and 300 g. of a 20% sodium hydroxide solution. The relative rates of addition are such that the pH is maintained between 7 and 11. When addition is complete, 61.5 g. of sodium acetate and 31.8 g. of sodium carbonate are added.

We claim:

1. An improved stable aqueous system which comprises (A) a hypohalite selected from the group consisting of hypochlorite, hypobromite and hypoiodite and (B) an N-hydrogen compound selected from the group consisting of succinimide, cyanamide, dicyandiamide, melamine, ethyl carbamate, urea, thiourea, 1,3 - dimethylbiuret, methyl phenylbiuret, isocyanuric acid, barbituric acid, 6-methyluracil, 2 - imidazolinone, iron, 5,5 - dimethylhydantoin, ethyleneurea, 2 - pyrimidinone, benzamide, phthalimide, N-ethylacetamide, azetidin - 2 - one, 2 - pyrrolidone, caprolactam, sulfamic acid, sulfamide, p-toluenesulfonamide, phenyl sulfinimide, phenyl sulfinimidylamide, diphenyl sulfonimide, dimethyl sulfinimine, isothiazolene - 1,1 - dioxide, orthophosphoryl triamide, pyrophosphoryl triamide, phenyl phosphoryl-bis dimethylamide, boric acid amide, methanesulfonamide, melamine, pyrrolidone, hydantoin, acetanilide, acetamide, N-methylurea, acetylurea, biuret, ethyl allophanate, pyrrole and indole in equilibrium with (C) the corresponding N-halo reaction product of hypohalite (A) and N-hydrogen compound (B); and (D) a sufficient amount of a weak acid selected from the group consisting of acetic acid, boric acid, arsenous acid, carbonic acid, phosphoric acids and silicic acids or the conjugate base of the weak acid as a buffer to maintain the pH of the system in a relatively stable range between 4 and 11 with the proviso that the reaction product (C) is present at a concentration of from  $1 \times 10^{-3}$  to 1.0 molar and the mol ratio of buffer to N-halo reaction product (C) is at least 1:10.

2. Improved system of claim 1 wherein the hypohalite is a hypochlorite.

3. Improved system of claim 1 wherein the hypohalite is sodium hypochlorite.

4. Improved system of claim 1 wherein the N-hydrogen compound (B) is sulfamic acid or an alkali or alkaline earth metal salt thereof and the corresponding N-halo reaction product (C) is N-monochloro, -bromo or iodo and N,N-dichloro, -dibromo or -diiodo sulfamic acid or the corresponding salts.

5. Improved system of claim 1 wherein the N-hydrogen compound (B) is a member of the group consisting of sulfamic acid, sulfamide, trisulfimide, p-toluenesulfonamide, melamine, sodium triamidometaphosphate, 5,5-dimethylhydantoin, methanesulfonamide, barbituric acid, 5-methyluracil, imidazolinone, pyrrolidone, acetanilide, acetamide, N-ethylacetamide, phthalimide, benzamide, succinimide, cyanamide, urea, N-methylolurea, N-methylurea, acetylurea, biuret, methyl allophanate, methyl carbamate, phthalohydrazide, pyrrole, indole, formamide, N-methylformamide.

6. Improved system of claim 1 wherein the buffer is an alkali metal or alkaline earth metal acetate, carbonate, phosphate, polyphosphate, borate, polyborate, silicate, polysilicate, or a combination of any two or more of these.

7. As a bleaching composition, an aqueous system of claim 1 in which the buffer is present in an amount sufficient to maintain the free hypochlorite concentration between  $0.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  moles per liter of laundry solution when the system is diluted with water about 500-1000 fold.

8. Improved system of claim 2 wherein the N-hydrogen compound (B) is sulfamic acid or an alkali or alkaline earth metal salt thereof and the corresponding N-halo

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reaction product (C) are N-monochloro-sulfamic acid or the corresponding salt in minor amount and N,N-dichlorosulfamic acid or the corresponding salt in major amount.

9. Improved system of claim 8 wherein the buffer 5 maintains the pH between 7 and 11.

10. Improved system of claim 9 wherein the hypochlorite is sodium hypochlorite.

11. As a bleaching composition, an aqueous system of claim 10 in which the buffer is present in an amount sufficient to maintain the free hypochlorite concentration 10 between  $0.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  moles per liter of laundry solution when the system is diluted with water about 500-1000 fold.

12. An improved stable aqueous system which comprises (A) a hypochlorite and (B) an N-hydrogen compound selected from the group consisting of sulfamic acid, sulfamide, trisulfimide, p-toluenesulfonamide, melamine, sodium trimidometaphosphate, 5,5 - dimethylhydantoin, methanesulfonamide, barbituric acid, 5 - methyluracil, 20 imidazolinone, pyrrolidone, acetanilide, acetamide, N-ethylacetamide, phthalimide, benzamide, succinimide, cyanamide, urea, N - methylolurea, N - methylurea, acetyl-

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urea, biuret, methyl allophanate, methyl carbamate, phthalohydrazide, pyrrole, indole, formamide, N-methylformamide in equilibrium with (C) the corresponding reaction product of hypochlorite (A) and N-hydrogen compound (B); and (D) a sufficient amount of an alkali metal or alkaline earth metal acetate, carbonate, phosphate, polyphosphate, borate, polyborate, silicate, polysilicate or a combination of any two or more of these to maintain the pH of the system in a relatively stable range between 4 and 11 with the proviso that the reaction product (C) is present at a concentration of from  $1 \times 10^{-3}$  to 1.0 molar and the mole ratio of buffer to N-halo reaction product (C) is at least 1:10.

## References Cited

## UNITED STATES PATENTS

3,170,883	2/1968	Owen et al. -----	252—187
3,328,294	6/1967	Self et al. -----	252—187 X

20 MAYER WEINBLATT, Primary Examiner

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252—99, 106, 187; 23—86; 210—62; 424—249

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,749,672 Dated July 31, 1973

Inventor(s) William C. Golton and Andrew F. Rutkiewicz

It is certified that error appears in the above-identified patent  
and that said Letters Patent are hereby corrected as shown below:

Column 12, line 19, "iron" should read --uron--.

Signed and sealed this 28th day of May 1974.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents