

[54] **RING HALOGEN-FREE SUBSTITUTED TRIAZINE COMPOUNDS AS BLEACH ACTIVATORS**

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[51] Int. Cl.² **C11D 7/54**

[58] Field of Search **252/102, 186**

[56] **References Cited**

UNITED STATES PATENTS

2,913,460	11/1959	Brown et al.	252/102
3,055,897	9/1962	Schwartz et al.	252/102
3,336,228	8/1967	Fuchs et al.	252/102
3,422,020	1/1969	Schmadel et al.	252/102
3,775,332	11/1973	Heins et al.	252/186

Primary Examiner—Benjamin R. Padgett

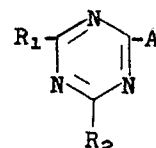
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[57] **ABSTRACT**

Ring halogen-free substituted triazine compounds of

the formula



where A is a radical selected from pyridinium, dialkoxyphosphinyl, mercapto, (dialkylthiocarbamoyl)thio, alkyl sulfonyl, trihalomethyl and sulfo-phenoxy radicals; and R₁ and R₂ individually represent hydroxy, mercapto, alkyl, alkenyl, alkoxy, alkylmercapto, aryl, aryloxy, arylmercapto, dialkoxyphosphinyl or

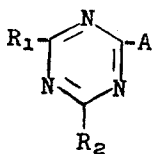


where R₃ and R₄ may be hydrogen, alkyl, cyanoalkyl, hydroxyalkyl, carboxyalkyl, chloroalkyl, alkoxyalkyl, sulfoalkyl, aryl, sulfoaryl, acylaminoaryl or carbamoylalkyl, or where R₃ and R₄ taken together may be joined to complete a heterocyclic ring selected from morpholine, piperazine and piperidine rings; are effective as bleach activators for peroxygen bleaching compositions.

10 Claims, No Drawings

RING HALOGEN-FREE SUBSTITUTED TRIAZINE COMPOUNDS AS BLEACH ACTIVATORS

This invention relates to bleaching compositions and more particularly to improved bleaching compositions comprising hydrogen peroxide or a hydrogen peroxide-releasing compound and as an activator for the peroxide-releasing compound a ring halogen-free triazine derivative represented by the formula:



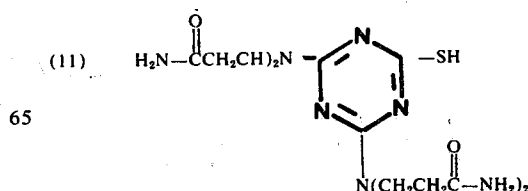
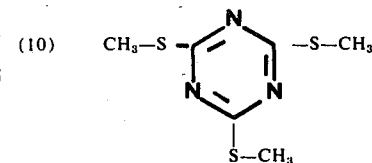
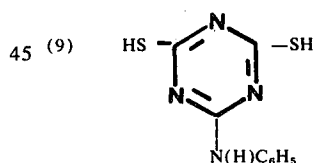
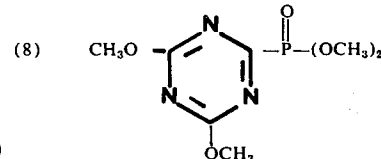
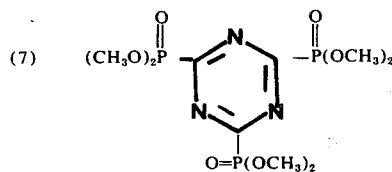
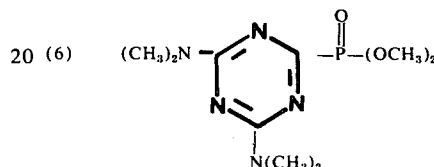
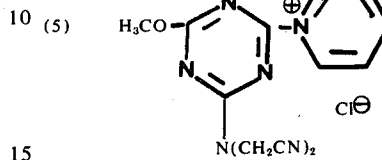
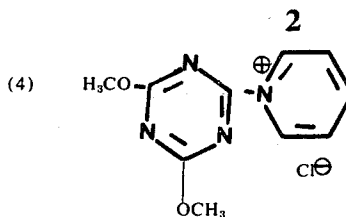
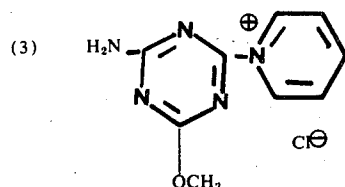
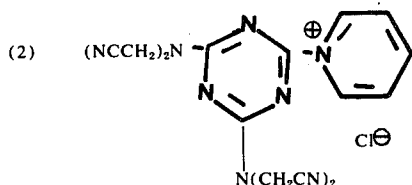
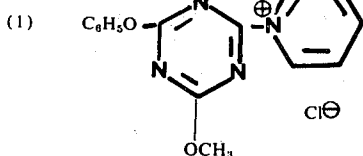
where A is a radical selected from pyridinium, dialkoxyposphinyl, mercapto, (dialkylthiocarbamoyl) thio, alkyl sulfonyl, trihalomethyl and sulfophenoxy radicals; and R₁ and R₂ individually represent hydroxy, mercapto, alkyl, alkenyl, alkoxy, alkylmercapto, aryl, aryloxy, arylmercapto, dialkoxyposphinyl or

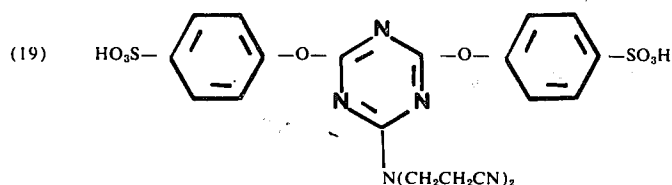
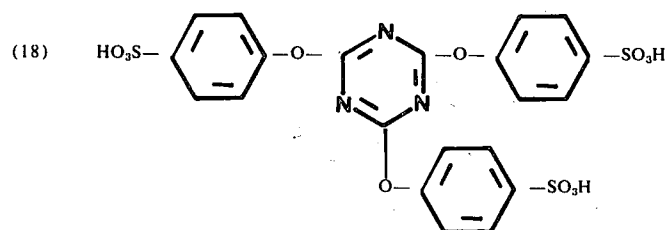
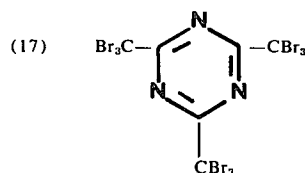
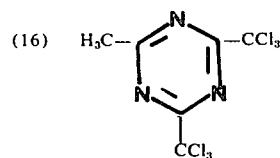
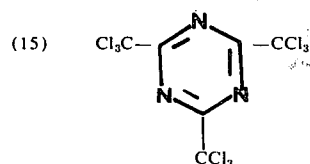
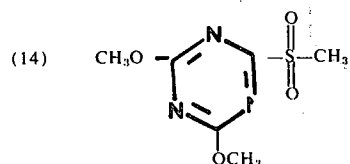
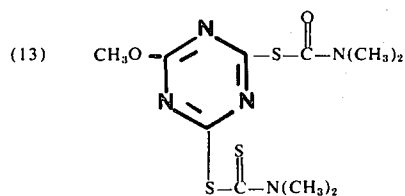
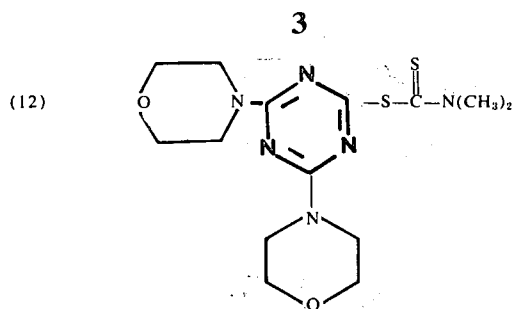


where R₃ and R₄ may be hydrogen, alkyl, cyanoalkyl, hydroxyalkyl, carboxyalkyl, chloroalkyl, alkoxyalkyl, sulfoalkyl, aryl, sulfoaryl, acylaminoaryl or carbamoylalkyl, or where R₃ and R₄ taken together may be joined to complete a heterocyclic ring selected from morpholine, piperazine and piperidine rings. In each instance where alkyl, alkenyl or alkoxy is mentioned, the term is intended to designate lower (i.e., C₁-C₅) alkyl, lower (i.e., C₁-C₅) alkenyl or lower (i.e., C₁-C₅) alkoxy.

Although the ring halogen-free triazine derivatives defined by the above formula are derivatives of s-triazines, similarly substituted derivatives of unsymmetrical triazine rings are also contemplated as activators for the bleach composition of the invention.

Typical halogen-free triazine compounds useful as bleach activators in the bleach compositions of this invention are the following.





The bleaching compositions of the invention contain the activating compound and the hydrogen peroxide-releasing compound in a molar ratio ranging from about 1:1 to about 1:10, respectively, with a preferred range of about 1:1 to 1:3. The actual ratio of activator to bleach can, of course, be varied widely for varying applications.

The oxygen bleaches useful in these bleaching compositions are hydrogen peroxide and organic peroxides and inorganic peroxygen salts that liberate hydrogen peroxide in water. Examples of peroxide bleaching compounds are urea peroxide, benzoyl peroxide, methyl ethyl ketone peroxide, and the like. Examples of inorganic peroxygen bleaching compounds are alkali metal perborates, percarbonates, perphosphates, persulfates, monopersulfates, and the like. Mixtures of two or more bleaching compounds can, of course, be used if desired.

Although the various peroxide releasing compounds as mentioned above may be used in the compositions of the invention, preferred peroxide-releasing compounds are sodium perborate (for economic considerations) and sodium percarbonate (for ecological considerations).

The activated bleach compositions of the invention are useful for bleach applications for various substrates including fabrics, particularly when incorporated with detergent compositions for household or commercial laundering purposes. A most important property of such detergent compositions is the ability to remove stains including food stains such as those of coffee, tea, wine and the like as well as to maintain purity of white in uncolored textiles. Aside from food stains, soiling in general may be removed such as grass stains, urine stains and the like.

In addition to the detergent, peroxygen-releasing compound and peroxygen bleach activator, such detergent compositions may contain other optional additives such as germicides, fungicides, enzymes, optical brighteners, colorants, perfumes, thickeners, emulsion or suspension stabilizers, and the like, including "builders," such as sodium phosphate, salts, carbonates, silicates, and the like as usually encountered in the art.

The detergent component of such activated bleach compositions may be any of the conventional types such as anionic, cationic, nonionic or amphoteric.

Examples of typically suitable anionic detergents include the alkali metal or alkaline earth metal salts of higher alkylbenzene sulfonates, olefin, sulfonates,

higher alkyl sulfates and higher fatty acid monoglyceride sulfates.

Examples of typically suitable cationic detergents include tetraalkyl ammonium salts in which one of the alkyl groups contains approximately 12 to 18 carbons such as dodecyltrimethylammonium chloride or ethyldimethyloctadecylammonium methosulfate.

Examples of suitably typical amphoteric detergents are those detergent compounds possessing both cationic and anionic sites and include, for example, amino fatty acids such as dimethylaminopropionic acid and iminodifatty acids such as methyliminodilauroic acid.

Examples of typical nonionic detergents include polyglycol ethers of alkanol amides of higher fatty acids and also polyglycol ethers of higher alkanols and higher fatty acids.

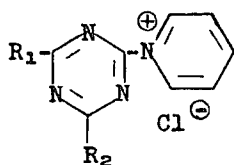
Bleaching compositions may generally be used also for their germicidal properties in various applications for control of microbial growth. Applications may be made to any surface or substrate where such control is desired.

The treatment of swimming pool water and swimming pool surfaces with the compositions of the invention is especially efficacious since the usually lower temperatures of these environments prevent effective use of other antimicrobial agents. A related utility is the treatment of water supplies to render the same fit for human consumption or for industrial use, such as the sanitization of field water for consumption by military personnel or the treatment of industrial process water so it can be reused in industrial processes or by the surrounding community. The compositions also may be employed in admixture with detergents for use as home or industrial germicidal detergents, or in hair bleaching compositions containing peroxygen compounds.

The following examples and tests will serve to further illustrate the invention.

EXAMPLES 1-3

Preparation of Pyridinium Compounds



To a solution of the respective di-functional monochloro triazine in 100 ml. ethyl acetate is added a molar equivalent of pyridine (using a slight excess). The solid product forms almost immediately. The slurry is stirred for 4 hours, filtered and dried. No recrystallization is necessary.

Ex. No.	R ₁	R ₂	Yield	M.P.
1	-N(CH ₂ CN) ₂	-N(CH ₂ CN) ₂	60%	246-248°C. dec.
2	CH ₃ O-	CH ₃ O-	74%	135-137°C. dec.
3	CH ₃ O-	-N(CH ₂ CN) ₂	67%	300°C.

Evaluation of Compounds as Bleach Activators

The compounds of Examples 1-3, plus additional compounds (Examples 4-6) were evaluated as activators applied with sodium perborate and a detergent. In the tests, the mole ratio of activator used to sodium perborate was 1:1.1.

The test procedure was as follows: Five-gram swatches of desized, 80 × 80 cotton fabric are stained with tea in the following manner. Five tea bags are placed in one liter of water and boiled for five minutes. The swatches are then immersed in the tea and the boiling is continued for another five minutes. The swatches are then removed from the tea, wrung out, dried at 200°-215°F., rinsed in cold water and again dried.

Two of the stained cotton swatches are placed in a stainless steel Terg-O-Tometer, a test washing machine, manufactured by U.S. Testing Company and used in the detergent trade for evaluation purposes. Forty grams of unstained cotton fabric and one liter of distilled water at 120°F. are then added so as to provide a typical household washing machine water to cloth ratio of about 20:1. There are then added 2.0 grams of "Tide" (an anionic alkylaryl sulfonate type detergent), 0.33 gram of anhydrous sodium perborate (or an equivalent of hydrated material) and the indicated amount of the activator compound. The Terg-O-Tometer is operated at 100 cycles per minute for fifteen minutes at a temperature of 120°F. The swatches are then removed, rinsed with cold water, and dried at room temperature.

Reflectance readings on the swatches are taken both before and after laundering using a Hunter Model 25-M Reflectometer with a blue filter. The swatches are backed with a white porcelain plate and read once on each side. Fluorescent effect is excluded from all readings.

The reflectance readings are averaged and the percent stain removal is obtained in accordance with the following formula in which R is the symbol for Reflectance:

$$\text{Total \% stain removal} = \frac{R(\text{bleached}) - R(\text{stained})}{R(\text{unstained}) - R(\text{stained})} \times 100$$

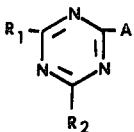
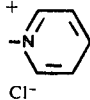
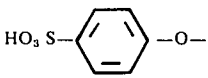
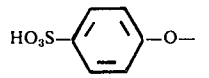
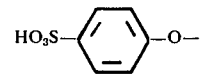
Control runs are also made for each set or series of evaluation tests using detergent and sodium perborate with no activator. The percent stain removed may vary somewhat on the Control due to variations in the cloth and the tea used to produce the stains.

The test results obtained are shown in Table I where the activator compounds are identified by the A, R₁ and R₂ radicals thereof in the general formula shown at the top of the Table.

Table I

Ex. No.	A	R ₁	R ₂	% Stain Removed (Control)	Wt. of Activator (g.)	% Stain Removed
1		-N(CH ₂ CN) ₂	-N(CH ₂ CN) ₂	35.9	1.10	44.9

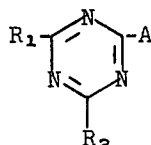
TABLE I - Continued

Ex. No.				% Stain Removed (Control)	Wt. of Activator (g.)	% Stain Removed
	A	R ₁	R ₂			
2		-OCH ₃	-OCH ₃	38.2	0.78	44.2
3		-OCH ₃	-N(CH ₂ CN) ₂	42.5	0.96	50.5
4	-P(OCH ₃) ₂ ⁽¹⁾	-P(OCH ₃) ₂	-P(OCH ₃) ₂	30.1	1.12	38.6
5	-SH ⁽²⁾	-SH	-NHC ₆ H ₅	29.3	0.71	50.9
6				34.9	1.98	49.7

⁽¹⁾Prepared according to J. Org. Chem. 22, 444 (1957)⁽²⁾Prepared according to J.C.S. 1967, C, 466.

We claim:

1. A bleaching composition comprising hydrogen peroxide or a hydrogen peroxide-releasing compound and an activating amount of a ring halogen-free triazine compound represented by the formula:



where A is a radical selected from the group consisting of pyridinium, dialkoxyphosphinyl, mercapto, (dialkylthiocarbamoyl)thio, alkyl sulfonyl, trihalomethyl and sulfophenoxy radicals; and R₁ and R₂ are individually selected from the group consisting of hydroxy, mercapto, alkyl, alkenyl, alkoxy, alkylmercapto, aryl, aryl-oxy, arylmercapto, dialkoxyphosphinyl and



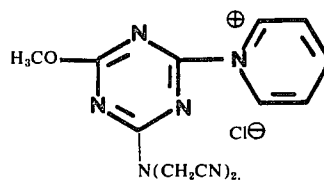
where R₃ and R₄ are individually selected from the group consisting of hydrogen, alkyl, cyanoalkyl, hydroxyalkyl, carboxyalkyl, chloroalkyl, alkoxyalkyl, sulfoalkyl, aryl, sulfoaryl, acylaminoalkyl and carbamoylalkyl, and where R₃ and R₄ taken together are joined to complete a heterocyclic ring selected from the group consisting of morpholine, piperazine and piperidine rings.

2. A composition according to claim 1 wherein the mole ratio of the ring halogen-free triazine compound to the hydrogen peroxide-releasing compound is from about 1:1 to about 1:10.

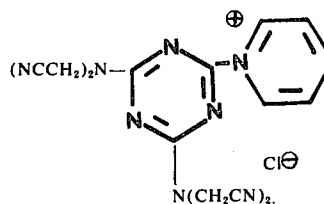
3. A composition according to claim 1 wherein the hydrogen peroxide-releasing compound is sodium perborate or sodium percarbonate.

4. A composition according to claim 1 wherein A in the ring halogen-free triazine compound is a pyridinium radical.

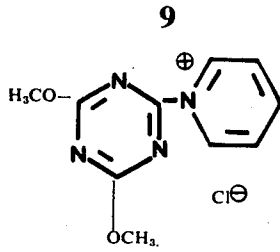
5. A composition according to claim 4 wherein the ring-halogen-free triazine compound is represented by the formula



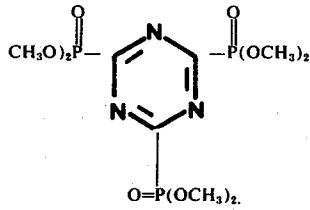
6. A composition according to claim 4 wherein the ring halogen-free triazine compound is represented by the formula



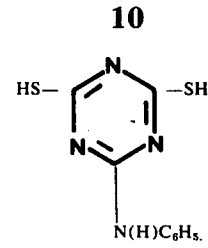
7. A composition according to claim 4 wherein the ring halogen-free triazine compound is represented by the formula



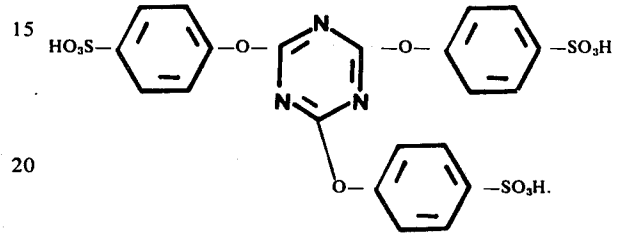
8. A composition according to claim 1 wherein the ring halogen-free triazine compound is represented by the formula



9. A composition according to claim 1 wherein the ring halogen-free triazine compound is represented by the formula



10. A composition according to claim 1 wherein the ring halogen-free triazine compound is represented by the formula



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