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3,532,634

BLEACHING COMPOSITIONS AND METHODS William G. Woods, Fullerton, Calif., assignor to United States Borax & Chemical Corporation, Los Angeles, Calif., a corporation of Nevada

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27 Claims 10

ABSTRACT OF THE DISCLOSURE

U.S. CI. 252-95

Activated persalt bleaching compositions containing an inorganic persalt, a water-soluble salt of a transition metal ¹⁵ having an atomic number of 24 to 29, inclusive, an oxidatively stable chelating agent and a persalt activator agent. The bleaching compositions can be formulated with the usual detergent materials to provide a detergent-persalt bleach combination. ²⁰

This application is a continuation-in-part of my copending application Ser. No. 530,789 filed Mar. 1, 1966, 25 now abandoned.

This invention relates to bleaching compositions and more particularly this invention relates to bleaching compositions and methods utilizing the inorganic persalt bleaching agents. 30

The inorganic persalts, especially sodium perborate, are well known as textile bleaching agents and find wide application in washing solutions, especially in the European countries. These compounds suffer from a major disadvantage, however, in that they require relatively high washing temperatures in order to obtain full benefit from the bleaching action of the persalt. This problem is especially pronounced in the United States where washing temperatures are relatively low.

Therefore, there has been proposed in the art the use ⁴⁰ of activators or accelerating agents which increase the bleaching action of the persalt at lower temperatures. Typical among these activating agents are the organic anhydrides such as succinic anhydride and phthalic anhydride, substituted phenyl esters of aliphatic acids such as sodium p-acetoxybenzenesulfonate and N,N-diacyl compounds. Although these activating agents are effective, they still do not activate the persalt sufficiently to obtain bleaching action comparable to that obtained by use of ⁵⁰ the chlorine-type bleaches at relatively low washing temperatures.

This invention provides novel bleaching compositions based on inorganic persalts which have excellent bleaching action at low washing temperatures, which is surprisingly comparable to the bleaching action obtained with the chlorine-type bleaches. Such activity has heretofore been impossible with the persalt type bleaching agents.

The bleaching compositions of this invention comprise a solid inorganic persalt bleaching agent, a water-soluble salt of a transition metal having an atomic number of from 24 to 29, inclusive, an oxidatively stable chelating agent, and a persalt activator agent. It has surprisingly been found that the present bleaching compositions are far superior to persalt bleaching agents activated by the heretofore known activating agents. The combinations of this invention provide a synergistic bleaching activity which is far better than that obtained by persalts activated with the single compounds.

The various ingredients of the bleaching composition are present in the bleaching solution in the following approximate molar proportions: 2

Persalt	about 1
Fransition metaldo.	0.0005-0.01
Chelating agentdo.	0.001-0.1
	0.05 1.5

Preferably the molar proportion is about 0.001-0.005 of transition metal to about 0.01-0.05 of the chelating agent to about 0.3-1.0 persalt activator to about 1 of the persalt.

The persalts applicable in the present composition are the solid inorganic persalt bleaching agents such as the alkali metal perborates, persulfates, percarbonates, perpyrophosphates and persilicates, the sodium and potassium salts being especially useful. Sodium perborate is the presently preferred persalt.

The transition metals applicable to the present invention are derived from the water-soluble salts of the transition metals having an atomic number of from 24 to 29, inclusive. Inorganic and organic salts such as the chlorides, sulfates, nitrates, perchlorates, acetates and watersoluble oxides of chromium, manganese, iron, cobalt, nickel, copper, and the like, are typical of the salts which are useful. Cobalt, manganese, and copper salts are especially useful and are presently preferred. The metal salts can be combined with certain of the chelating agents to form salts or neutral compounds which serve to provide both the metal and the chelating agent in the compositions. Such combinations are also included within the scope of the invention.

The chelating agents applicable to the present invention are those which are oxidatively stable, that is, those which are not readily oxidized in the bleaching solution. These chelating agents preferably have a first complex formation constant with the transition metal ion of log 2 to about log 10 at about 20° C. See "Stability Constants of Metal-Ion Complexes," Chemical Society (London), Special Publication No. 17, 1964. Typical chelating agents which can be used are pyrrolidine-2-carboxylic acid, pyridine-2,6-dicarboxylic acid, picolinic acid, dipicolinic acid, 40 6-methylpicolinic acid, isonicotinic acid, quinolinic acid, isocinchomeronic acid, 1,10-phenanthroline and the alkyl substituted derivatives thereof, 2,2'-bipyridine, and the like. These chelating agents form complexes with the transition metals which are oxidatively stable. Well known chelating agents such as ethylenediaminetetraacetic acid and 1,2 - diaminocyclohexane-N,N,N',N'-tetraacetic acid, have complex formation constants with the instant metal ions of above log 10, and are unsuitable in the present bleaching compositions.

⁵⁰ The persalt activators are the well-known accelerators or activating agents for persalt bleaching agents, such as the organic acid anhydrides, phenyl esters of aliphatic acids having electronegative substituents on the phenyl ring, N,N-diacyl compounds, and acylcyanurates. Typical activating agents suitable for the present compositions are the following:

Anhydrides:

succinic anhydride phthalic anhydride adipic anhydride maleic anhydride chlorobenzoic anhydride benzoic anhydride glutaric anhydride acetic anhydride isophthalic anhydride

Such anhydrides can be defined as preferably being derived from:

(a) aliphatic monocarboxylic acids of one to about six carbon atoms,

- (b) aliphatic dicarboxylic acids of 3 to about 12 carbon atoms, or
- (c) mono and dicarboxylic acids of benzene.

Esters:

sodium p-acetoxybenzenesulfonate

acetylsalicyclic acid

- chloroacetylsalicyclic acid
- sodium p-butyroxybenzenesulfonate
- p-acetoxybenzoic acid
- chloroacetylphenol-4-potassium sulfonate 3,4,5-tri(chloroacetyl)gallic acid

These esters can be defined preferably as phenyl esters of aliphatic acids of up to about 5 carbon atoms having electronegative substituents on the phenyl ring, said sub-15 stituents being selected from the carboxyl groups and sulfonic acid groups. The carboxyl and sulfonic acid groups can be in the form of either the free acids or salts. Also, the aliphatic acid moiety can be halogenated such as in the case of chloroacetyl. See British 20 Pat. 864,798 and U.S. Pat. 3,130,165 for other typical examples.

- N,N-diacyl compounds: N,N-diacetylaniline tetraacetylmethylenediamine triacetylmethylenediamine tetraacetylhydrazine
- N,N-diacyl compounds: tripropionylhydrazine N,N-diacetyl-N'-benzoylhydrazine tetraacetylhexamethylenediamine N,N-diacetyl-p-toluidine N,N-diacetyl-p-chloroaniline N,N-dibutyrylaniline triacetylhydrazine tetraacetylethylenediamine Acylcyanurates: triacetylcyanurate tripropionylcyanurate diacetylcyanurate

dicyclohexanoylcyanurate

The N,N-diacyl compounds and acylcyanurates can be defined as preferably N-acylated anilines, hydrazines, lower alkylenediamines (preferably with 1–6 carbon atoms in the alkylene group) and cyanurates in which the acyl moiety has up to about 6 carbon atoms. See U.S. Pat. Nos. 3,163,606 and 3,332,882 for typical examples of this class of compounds.

The activating agents generally have some solubility in 5 the aqueous bleaching solution. However, since only very small amounts are employed, a very slight water solubility is all that is required.

The textile materials to be bleached are treated with the bleaching composition in aqueous solution. Preferably, 5 the bleaching compositions are formulated with detergents and/or other laundry additives such as water softeners, antiredeposition agents, corrosion inhibitors, and the like. Therefore, also provided by this invention are laundry detergent compositions comprising one or more 6 synthetic organic detergents or soaps and the bleaching compositions. Such detergent formulations provide a superior fabric washing composition for use at moderate washing temperatures. The bleaching action provided by the bleaching composition is equivalent to that obtained 6 by use of chlorine-type bleaches, such as sodium hypochlorite and the chlorinated cyanuric acids.

The following examples are presented to illustrate this invention but the invention is not to be considered restricted to the specific examples given.

EXAMPLE I

Washing tests using various activator compositions were conducted with Tide, a commercially available heavy duty detergent, and sodium perborate. The washing solutions 75

contained 0.1% Tide and 0.125% sodium perborate. The tests were conducted using a Model 7243 Terg-O-Tometer apparatus, manufactured by U.S. Testing Company, Inc., Hoboken, N.J. This apparatus consists of four 2000 ml. stainless steel beakers immersed in a constant temperature water bath maintained at 120° F. Each beaker is fitted

with a stainless steel agitator which is set to oscillate at 150 r.p.m. in these tests.

The procedure involves adding 750 ml. of distilled water to the beaker and allowing the system to equilibrate at the desired temperature. Tide detergent (0.75 grams: 0.1%) then is added with agitation. After 1 minute of agitation, three swatches of cloth, 4 x 5 inches, are added. With continuous agitation, the desired reagents are added at 1 minute intervals and the agitation continued for 15 minutes after the last reagent is added. The switches then are removed from the wash solution, shaken with 400 ml. of distilled water, squeezed by hand, further rinsed in a running stream of distilled water 20 on both sides, wrung by hand, and then ironed on the nonreflectance side.

Reflectance measurements were made before and after washing using Gardner Laboratories Multi-Purpose Reflectometer No. 1478 with a green filter. Standard tile

²⁵ Ser. No. R-2712-59 (64.1 reading) was used with unbleached muslin samples and standard tile No. R-2717-59 (14.5 reading) was used with the EMPA cotton Bleach Test Cloth #1, Testfabrics, Inc., New York, N.Y. The percentage increase in reflectance was calculated as follows:

Percent increase =

$\frac{\text{(initial reflectance)-(final reflectance)}}{\text{(initial reflectance)}} \times 100$

The increases are averaged for the three swatches in each run and reported as the mean. The increase in reflectance attributed to the activator system was calculated by taking the percent increase in reflectance obtained with the persalt activator, chelated metal ion, or combinations thereof, and subtracting the percent increase obtained by sodium perborate alone (15.5). The difference is the percent increase in reflectance attributed to the activator system and was expressed as Reflectance Increase. The results are recorded in Table I in which the amounts repre-45 sent the concentration of activator ingredients expressed as millimoles per liter.

TABLE I

50	No.	Activator system	Amount	Reflect- ance increase
	1	Acetic anhydride	8, 14	23.7
	2	do	4. 07	7.6
	3	Succinic anhydride Sodium p-acetoxybenzenesulfonate	8, 12	-2.3
	4	Sodium p-acetoxybenzenesulfonate	12.21	19.0
	5	do	8, 14	13.4
55	6	do	1.63	-1.5
00	7	Tetraacetylhydrazine	16.2	26.3
	8	do	12.0	12.6
	9	do	8.1	4.4
	10	Trisacetylcyanurate	8.13	10.0
	11	Phthalic anhydride	8.14	1.0
	12	Cobaltous chloride	0.03)	7.2
		Picolinic acid	0,25 🖇	1. 4
60	13	Acetic anhydride Cobaltous chloride	8.14 j	
		Cobaltous chloride	0.03	115.7
		Picolinic acid	0.25	
	14	Succinic anhydride	8. 12 j	
		Cobaltous chloride	0.03	23.1
		Picolinic acid	0.25	
	15	Sodium p-acetoxybenzenesulfonate	8.14)	
65		Cobaltous chloride	0.03	92.0
00		Picolinic acid	0.25	
	16	Phthalic anhydride	8.14 j	
		Cobaltous chloride.	0,03	16.0
		Picolinic acid	0, 25	
	17		16.2 j	
		Cobaltous chloride	0.03	149.8
		Picolinic acid	0,25	
70	18	Tetraacetvlhvdrazine	8.1)	
		Cobaltous chloride	0.015	106.3
		Picolinic acid	0.25	
	19	Triacetyleyanurate	8. 13 Ĵ	
		Cobaltous chloride	0.03	96.4
		Picolinic acid	0.25	
	20	Ferrous sulfate	0.03)	
75		2,6-dicarboxypyridine	0.25	-1, 5
75		,	5, 20)	

put.	
F _	

	C			
,			Reflect-	
			ance	
No.	Activator system	Amount	increase	
21	Acetic anhydride	4 07 1		
<i>4</i> 1,	Ferrous sulfate	4.07 0.03	12.8	~
	2,6-dicarboxypyridine	0.25		5
22	_ Sodium p-acetoxybenzenesulfonate	8.14		
	Ferrous sulfate 2,6-dicarboxypyridine	0.03	29.9	
23	_ Cobaltous chloride	0. 03 1	1.0	
	1,10-phenanthroline	0.275	. 1.0	
24	Acetic anhydride Cobaltous chloride	$8.14 \\ 0.03$	 124.9 	10
	1,10-phenanthroline	0.275	124, 5	
25	. Sodium p-acetoxybenzenesulfonate	8.14		
	Cobaltous chloride 1,10-phenanthroline	$0.03 \\ 0.275$	· 157.4	
26	_ Tetraacetylhydrazine	12.0		
	Cobaltous chloride	0,03	· 134.3	-
27	1,10-phenanthroline	0.275		15
41	Sodium p-acetoxybenzenesulfonate Cobaltous chloride	1,63 0,03	101.5	
	1,10-phenanthroline	0.268	20200	
28	Sedium p-acetoxybenzenesulfonate Cobaltous chloride	12.21		
	1,10-phenanthroline	0,03 0,268	57.4	
29	_ Cupric sulfate	0.03		20
	2.2'-bynyridine	0.25	2.9	20
30	_ Acetic anhydride	$\left. \begin{array}{c} 8.14 \\ 0.03 \end{array} \right\}$	05 5	
	Cupric sulfate	0, 05	- 35, 5	
31	2,2'-bipyridine Sodium p-acetoxybenzenesulfonate	8.14	i i	
	Cupric sulfate	0.015	25.1	
32	2,2'-bipyridine Cupric sulfate	0.25 0.03		25
02	Piconlinic acid	0.25	-1.5	20
33		8.14		
	Cupric sulfate Picolinic acid	0.03 0.25	· 25.0	
34	Cupric sulfate	0. 03		
	1,10-phenanthroline	0.275	6.4	
35	Sodium p-acetoxybenzenesulfonate Cupric sulfate	8.14	- 39.3	30
	1,10-phenathroline	0.275	. 99.9	
36	Manganous sulfate	0,03)	. 0	
07	Picolinic acid Acetic anhydride	0.25 (8.14)	U	
37	Manganous sulfate	0.03	71.9	
	Picolinic acid	0.25	1210	
38	Nickel acetate	0.03	0.6	35
20	Picolinic acid Acetic anhydride	0.25 f 8.14		
	Nickel acetate	0.03	43, 5	
	Picolinic acid Cobaltous chloride	0.25		
40	2,2'-bipyridine	$\left. \begin{array}{c} 0.03 \\ 0.25 \end{array} \right\}$	1.4	
41	_ Sodium p-acetoxybenzene sulfonate	8, 14		40
	Cobaltous chloride	0.03	151.3	40
42	2,2'-bipyridine Trisacetylcyanurate	0.25 J 8.13		
44	Cobaltous chloride	0.03	137.1	
	2,2'-bipyridine	0.25	2011 2	
43	Acetic anhydride	6.51		
	Cobaltous chloride	$\begin{array}{c} 0.024 \\ 0.2 \end{array}$	· 159.0	
44 1	Acetic anhydride	6, 51)		45
	Cobaltous chloride	0.024	64.4	
	2,2'-bipyridine	0, 2		
1 Mont N	Jo. 44 was in the absence of Tide			

¹ Test No. 44 was in the absence of Tide.

EXAMPLE II

The procedure of Example I was followed except 2.02 grams of potassium monopersulfate were employed instead of sodium perborate. The following results were obtained.

TABLE II	
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	Activator system	Amount	Reflect- ance increase
Number:			
45	Acetic anhydride	8,14	2
46	Picolinic acid	$\left. \begin{array}{c} 0.03 \\ 0.25 \end{array} \right\}$	7
47	Acetic anhydride Cobaltous chloride Picolinic acid	$\left. \begin{array}{c} 8.14 \\ 0.03 \\ 0.25 \end{array} \right\}$	13

Thus, as illustrated in the above examples, the synergized persalt bleaching compositions according to the present invention are surprisingly far superior to persalt bleaches activated by the usual activators or combinations of metal salts with chelating agents. For example, No. 13 gave a reflectance increase of 115.7; yet, the sum of the increase from the ingredients (Nos. 1 and 12) was only 30.9. Furthermore, such superior performance is obtained at a relatively low water temperature of 120° F.

suitable detergent formulations containing the bleaching systems of the present invention.

Detergent compositions were formulated by known procedures to provide two typical compositions.

5	Component: Parts by weight
	Sodium dodecylbenzenesulfonate 5
	Sodium lauric acid isoethioniate 2
	Lauryl alcohol 0.5
	Monoethanolamide of coconut oil fatty acid 0.5
10	Sodium tripolyphosphate 40
	Sodium silicate 3
	Carboxymethyl cellulose1
	Sodium sulfate 38
	Water 10
15	Optical brightener 1.01
	The above will be referred to hereafter as Detergent A. As an example of a typical nonionic detergent:

	Component: Parts by weight
0	Nonylphenyl condensed with 9 molecules of
	ethylene oxide 8
	Sodium tripolyphosphate 40
	Sodium silicate 5
	Carboxymethyl cellulose 1
5	Sodium sulfate 43
	Water 3
	Optical brightener 0.01

The latter formulation will be denoted as Detergent B. Several methods can be used in the formulation of the compositions of this invention. It is preferred that the packaging arrangement be such that the unchelated metal salt is separated from the persalt in order to avoid catalytic decomposition of the persalt before use. The organic activators generally are subject to hydrolysis because of their high reactivity and, consequently, these activators should be protected from environmental moisture.

Several methods of so protecting the organic activator can be used, one of which is encapsulation. Solid particles or liquid droplets can be encapsulated with coatings which dissolve or disperse under conditions of use. Suitable encapsulating materials include gelatin, ethyl cellulose, emulsifiable waxes, and the like. Such an encapsulated activator, in the form of solid particles, can be intermixed with a granulated detergent formulation and the persalt, the chelating agent, and the metal salt. The metal salt preferably should be combined wih the activator and encapsulated or it should be reacted with the chelating agent prior to combination with the detergent and persalt.

The following is a typical packaging arrangement.

Part I: Parts I	by weight
Detergent A granules	100
Sodium perborate tetrahydrate	50
Picolinic acid	1.2

⁵⁵ Part II:

Sodium p-acetoxybenzenesulfonate	77
Cobaltous sulfate (anhydrous)	0.2

Components of Part II are intimately mixed and en-60 capsulated by well-known methods. Parts I and II then are thoroughly intermixed to give a free-flowing solid composition, useful in home laundry applications. This composition also may be compressed into tablets.

A second method involves the use of composite tablets 65 which contain the detergent, persalt, activator, metal ion, and chelating agent in various configurations. For example, a core is prepared consisting of a pellet of a compressed, intimate mixture of 20 grams of tetraacetylhydrazine, 0.06 gram of anhydrous cobaltous sulfate, 0.5 gram of starch, and 0.1 gram of talc. This core is sur-70rounded by a coating of a mixture of 60 grams of Detergent A, 15 grams of sodium perborate tetrahydrate and 0.5 gram of 1,10-phenanthroline. Another tablet configuration can be used in which a compressed cylindrical body The following examples illustrate the preparation of 75 comprising 60 grams of Detergent B mixed with 0.56 gram

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of 2,2'-bipyridine contains two separate plugs imbedded in it, one of which comprises 15 grams of sodium perborate and the other 8.3 grams of triacetylcyanurate mixed with 0.05 gram of anhydrous cobaltous chloride.

A third method of formulating the compositions of this $\mathbf{5}$ invention involves the use of two separate packets made of polymeric film such as polyethlene, polyethylene terephthalate, polyvinyl chloride, ethyl cellulose, and the like. One of the packets contains the organic activator and metal salt, while the other contains the detergent, the 10persalt, and the chelating agent. The following is a typical example.

Packet I: G	rams	
Detergent B	60	
Sodium perborate tetrahydrate	15	1
Picolinic acid	0.4	
Packet II:		
Acetic anhydride	10	

Manganous acetate _____ 0.06

In practice, both packets are opened and the contents 20simultaneously poured into about 12 to about 18 gallons of water to be used for the washing and bleaching operation.

What is claimed is:

1. A bleaching composition consisting essentially of a 25 solid, inorganic persalt bleaching agent, a water soluble salt of a transition metal having an atomic number of from 24 to 29, inclusive, an oxidatively stable chelating agent having a first complex formation constant with said transition metal ion of log 2 to log 10 at about 20° C., and a persalt activator agent, the components of said bleaching composition being present in a molar proportion of:

Persalt	About 1	
Transition metal	About 0.0005-0.01	3
Chelating agent	About 0.001-0.1	
Persalt activator	About 0.05–1.5	

said persalt activator agent being selected from

- (a) the organic anhydrides derived from alkyl and 40 alkenyl monocarboxylic acids of 1 to about 6 carbon atoms, alkyl and alkenyl dicarboxylic acids of 3 to about 12 carbon atoms or mono- or dicarboxylic acids of benzene,
- (b) phenyl esters of alkyl and haloalkyl carboxylic 45acids of up to about 5 carbon atoms having electronegative substituents on the phenyl ring, said substituents being selected from the carboxyl and sulfonic acid groups, or
- (c) N-acyl compounds selected from N-acylated 50anilines, hydrazines, lower alkylenediamines, and cyanurates in which the acyl moiety has up to about 6 carbon atoms.

2. A detergent composition consisting essentially of a water-soluble anionic or nonionic synthetic organic de-55tergent or soap and the bleaching composition of claim 1. 3. A bleaching composition according to claim 1 in

which said persalt is sodium perborate.

4. In the method of bleaching textiles by treating said textiles with an aqueous solution of a normally solid in-60 organic persalt bleaching agent, the improvement which comprises activating said bleaching agent with a combination of a water-soluble salt of a transition metal having an atomic number of from 24 to 29, inclusive, an oxidatively stable chelating agent having a first complex formation constant with said transition metal ion of log 2 to log 10 at about 20° C., and a persalt activator agent in amounts sufficient to provide the following molar proportions:

Persalt	About 1	
Transition metal	About 0.0005-0.01	
Chelating agent	About 0.001-0.1	
Persalt activator	About 0.05-1.5	

said persalt activator agent being selected from:

alkenyl monocarboxylic acids of 1 to about 6 carbon atoms, alkyl and alkenyl dicarboxylic acids of 3 to about 12 carbon atoms or mono- or dicarboxylic acids of benzene,

- (b) phenyl esters of alkyl and haloalkyl carboxylic acids of up to about 5 carbon atoms having electronegative substituents on the phenyl ring, said substituents being selected from the carboxyl and sulfonic acid groups, or
- (c) N-acyl compounds selected from N-acylated anilines, hydrazines, lower alkylenediamines, and cyanurates in which the acyl moiety has up to about 6 carbon atoms.

5. The method according to claim 4 in which said 15 persalt is sodium perborate.

6. A bleaching composition consisting essentially of a solid, inorganic persalt bleaching agent, a water-soluble salt of a transition metal having an atomic number of from 24 to 29, inclusive, an oxidatively stable chelating agent having a first complex formation constant with said transition metal ion of log 2 to log 10 at about 20° C., and a persalt activator agent, the components of said bleaching composition being present in a molar proportion of

Persalt	About 1
Transition metal	About 0.0005-0.01
Chelating agent	About 0.001-0.1
Persalt activator	

 $_{30}$ said persalt activator agent being selected from the group consisting of succinic anhydride, phthalic anhydride, adipic anhydride, benzoic anhydride, glutaric anhydride, acetic anhydride, sodium p-acetoxybenzene-sulfonate, acetylsalicylic acid, cholroacetylsalicylic acid, sodium pbutyroxybenzenesulfonate, p-acetoxybenzoic acid, N,N-35diacetylaniline, tetraacetylmethylenediamine, triacetylmethylenediamine, tetraacetylhydrazine, triacetylcyanurate, tripropionylcyanurate and diacetylcyanurate.

7. A bleaching composition according to claim 6 wherein the components are present in the following molar proportions:

Persalt	About 1
Transition metal	About 0.001-0.005
Chelating agent	
Persalt activator	About 0.3–1.0

8. A bleaching composition according to claim 6 wherein said persalt is sodium perborate.

9. A bleaching composition according to claim 6 wherein said transition metal is cobalt.

10. A bleaching composition according to claim 6 wherein said transition metal is manganese.

11. A bleaching composition according to claim 6 wherein said transition metal is copper.

- 12. A bleaching composition according to claim 6 wherein said persalt activator is acetic anhydride.
- 13. A bleaching composition according to claim 6 wherein said persalt activator is sodium p-acetoxybenzenesulfonate.
- 14. A bleaching composition according to claim 6 wherein said chelating agent is picolinic acid.

15. A bleaching composition according to claim 6 wherein said chelating agent is 1,10-phenanthroline.

16. A bleaching composition according to claim 6 65 wherein said persalt is potassium monopersulfate.

17. A bleaching composition according to claim 6 wherein said persalt activator is triacetylcyanurate.

18. In the method of bleaching textiles by treating said textiles with an aqueous solution of a normally solid 70 inorganic persalt bleaching agent, the improvement which comprises activating said bleaching agent with a combination of a water-soluble salt of a transition metal having an atomic number of from 24 to 29, inclusive, an oxidatively stable chelating agent having a first complex formation (a) the organic anhydrides derived from alkyl and 75 constant with said transition metal ion of log 2 to log 10

at about 20° C., and a persalt activator agent in amounts sufficient to provide the following molar proportions:

Persalt	About 1
Transition metal	About 0.0005-0.01
Chelating agent	About 0.001–0.1
Persalt activator	About 0.05-1.5

said persalt activator agent being selected from the group consisting of succinic anhydride, phthalic anhydride, adipic anhydride, benzoic anhydride, glutaric anhydride, 10acetic anhydride, sodium p-acetoxybenzenesulfonate, acetylsalicylic acid, chloroacetylsalicylic acid, sodium p-butyroxybenzenesulfonate, p-acetoxybenzoic acid, N,Ndiacetylaniline, tetraacetylmethylenediamine, triacetylmethylenediamine, tetraacetylhydrazine, triacetylcyanu- 15 phenanthroline. rate, tripropionylcyanurate and diacetylcyanurate.

19. The method according to claim 18 in which said persalt is sodium perborate.

20. The method according to claim 18 wherein the components are present in the following molar $_{20}$ agent, are dissolved in said aqueous solution. proportions:

Persalt	About 1	
Transition metal	About 0.001-0.005	
Chelating agent	About 0.01–0.05	
Persalt activator	About 0.3–1.0	25

21. The method according to claim 18 in which persalt is potassium monopersulfate.

22. In an aqueous persalt bleaching solution of a normally solid, inorganic persalt bleaching agent activated 30 by about 0.05-1.5 mole of persalt activator per mole of said persalt bleaching agent, the improvement which comprises a synergistic amount of about 0.0005-0.01 mole of a water soluble-salt of a transition metal having an atomic number of from 24 to 29, inclusive, and about 0.001-0.1 35 mole of an oxidatively stable chelating agent having a first complex formation constant with said transition metal ion of log 2 to log 10 at about 20° C., dissolved in said aqueous solution, said molar amounts being based on one mole of said persalt bleaching agent and said 40 8-111; 252-99, 186

persalt activator being selected from the group consisting of succinic anhydride, phthalic anhydride, adipic anhydride, benzoic anhydride, glutaric anhydride, acetic anhydride, sodium p-acetoxybenzenesulfonate, acetylsalicylic acid, chloroacetylsalicylic acid, sodium p-butyroxybenzenesulfonate, p-acetoxybenzoic acid, N,N-diacetylaniline, tetraacetylmethylenediamine, triacetylmethylenediamine, tetraacetylhydrazine, triacetylcyanurate, tripropionylcyanurate and diacetylcyanurate.

23. A bleaching composition according to claim 22 in which said persalt bleaching agent is sodium perborate.

24. A bleaching solution according to claim 22 wherein said persalt activator is triacetylcyanurate, said transition metal is cobalt and said chelating agent is 1,10-

25. A bleaching solution according to claim 22 wherein about 0.001-0.005 mole of said water-soluble salt of a transition metal and 0.01-0.05 mole of said oxidatively stable chelating agent, per mole of said persalt bleaching

26. A bleaching solution according to claim 22 wherein said oxidatively stable chelating agent is picolinic acid.

27. A bleaching solution according to claim 25 wherein said transition metal is cobalt and said chelating agent is 5 1,10-phenanthroline.

References Cited

UNITED STATES PATENTS

3,156,654	11/1964	Konecny et al.
3,163,606	12/1964	Viveens et al.
3,177,148	4/1965	Bright et al.
3,211,658	10/1965	Hirtz et al.
3,332,882	7/1967	Blumbergs et al.
3,338,839	8/1967	MacKeller et al.

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