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PROCESS FOR THE TREATMENT OF FIBROUS MATERIALS

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The present invention relates to improvements in the treatment of natural or synthetic fibers and textiles produced therefrom with peroxidic compounds, such as hydrogen peroxide, perborates, percarbonates and perpyrophosphates, and more particularly to a method in which the peroxide treatment is especially effective at temperatures below the boiling point of the aqueous peroxidic solutions employed, for example, between 50 and 80° C.

In peroxidic textile treating baths for washing and bleaching purposes, it has usually been necessary to raise the temperature of such baths substantially up to their boiling point in order that satisfactory washing and bleaching effects be obtained. The high temperatures required are disadvantageous, as normal hot water supplies in households are such that washing operations are normally carried out at temperatures of about 60 to 70° C., unless boilers are used.

It is therefore an object of the invention to provide a manner in which peroxidic compositions can be rendered more effective in the treatment of textiles at temperatures substantially lower than the boiling point of the aqueous solutions employed.

According to the invention, it was unexpectedly found that the presence of organic compounds containing one or more nitrile groups accelerate the liberation of oxygen from substances containing active oxygen (peroxidic compounds) and to increase the cleaning action to such an extent that the same cleaning action is obtained at, for example, 60° C., as in the usual "boil" washes. Therefore, in carrying out the invention, nitriles are added to the washing liquid containing peroxidic compounds. Very good results are obtained with stoichiometric portions of the nitriles and the peroxidic compounds, that is, 1 mol mononitrile per mol of peroxide. Di- and polynitriles as a result have an increased action corresponding to the number of nitrile groups contained therein. However, the invention is not limited to this molar relationship, as the regulation of the washing velocity must be more suited to the practical requirements than to the chemical requirements.

Organic nitriles, whether mono-, di- or polynitriles, are suitable for the purposes of the invention, as long as they still can be dissolved or suspended in water and are not absolutely insoluble. They can be of aliphatic, aromatic, aliphatic-aromatic, or hydroaromatic nature and the C chains or rings of such compounds may be interrupted by heteroatoms. The best results are obtained with organic nitriles containing a plurality of nitrile groups which are not separated too far from each other. The activity increases to a certain extent with increase in nitrile group content. On the other hand, cyanides, that is, salts of hydrocyanic acid, are not suitable, as they tend to discolor textiles.

In contrast to such known processes in which the decomposition of peroxidic compounds is accelerated with metal salts or organic metal compounds, the present invention has the advantage that in the absence of metals

the catalytic damage of textiles observed in peroxide baths containing metal compounds is completely avoided. For this reason, metal compounds were never successfully introduced into bleaching practices. Furthermore, such metal compound accelerators usually led to soiling of the textiles rather than an improved washing effect.

The following organic nitrile compounds have been found particularly effective as additions in aqueous washing and bleaching baths containing peroxidic compounds:

Malonitrile
Malonic acid amide nitrile
Ethylene dinitrile
Ethylene diamino tetracetic acid nitrile
Tetramethylene dinitrile
Nitrilotriacetic acid nitrile
Benzonitrile
Dimethyl-diamino-succinic acid dinitrile
Methylene-bis-imino acetonitrile
Phthalonitrile
Terephthalic acid nitrile

The activation of the peroxidic compounds in bleaching and washing baths according to the invention is obtained even in the presence of the usual stabilizers, such as sodium pyrophosphate, sodium silicate or magnesium silicate and the like. Also, soaps, wetting agents and chemicals which regulate the pH of the baths can be present. Furthermore, it is also advantageous to employ fiber protection agents in combination therewith. The components indicated can, if desired, be combined in a washing powder ready for use.

The following examples will serve to illustrate several modifications according to the invention:

Example 1

An aqueous washing bath was prepared which, per liter, contained the following composition:

10 g. sodium soap
2 g. sodium pyrophosphate
0.7 g. sodium perborate
0.1 g. malonitrile

Soiled cotton underwear was washed in such bath at 60° C. with moderate movement. The ratio of underwear to bath was 1:20. After 1 hour, a washing action was achieved which corresponded to that achieved with a boil wash of the same duration (without the malonitrile) in which the bath was slowly heated to the boiling point. Knitted goods washed in the same way exhibited the same whiteness grade.

Example 2

Cotton nettle cloth soiled with tomato juice was treated in the following washing bath at 60° C.:

Per liter—
10 g. sodium soap
2 g. sodium pyrophosphate
0.5 g. sodium perborate
0.3 g. malonic acid amide nitrile

The ratio of cloth to bath was 1:15.

In comparison, nettle cloth containing the same soil was washed in a bath of the same composition but omitting the malonic acid amide nitrile while slowly heating the bath to its boiling point. It was found that nettle cloth washed at 60° C. with the bath containing malonic acid amide nitrile was decolorized just as much as that which had undergone the boil wash.

The active oxygen content of the activated bath according to the invention diminished approximately in the same manner as in the boil wash, as can be seen from the following table for the indicated baths, each

having an initial active oxygen content of 0.056 g. (100%) per liter.

Bath	Active oxygen content of bath after—		
	30 min.	60 min.	120 min.
	Percent	*Percent*	*Percent*
(a) Activated bath at 60° C	45	31	17
(b) Unactivated bath boil wash	62	35	18
(c) Unactivated bath at 60° C	90	86	79

Example 3

A regenerated cellulose staple fiber fabric which was soiled with cherry juice was treated at 65° C. for two hours with a fabric to bath ratio of 1:20 in the following wash bath:

Per liter—
- 10 g. Marseilles soap
- 2 g. sodium pyrophosphate
- 2 g. sodium perborate
- 0.3 g. ethylene dinitrile

As a comparison, the same soiled fabric was given a boil wash in a bath of the same composition, but omitting the ethylene dinitrile.

The original activated oxygen content of 0.22 g. of the baths used in both washes diminished in the same manner, as can be seen from the following table:

Bath	Active oxygen content of bath after—		
	30 min.	60 min.	120 min.
	Percent	*Percent*	*Percent*
Activated bath at 65° C	57	41	28
Unactivated bath boil wash	62	38	29

The soil removed in the activated bath at 65° C. was as good as in the boil wash.

Example 4

25 kg. of Perlon fabric were subjected to a bleach upon a jigger in a bleaching bath containing N-phenylbiguanide as a protective agent for the polyamide fibers, both in the presence and absence of iminodiacetonitrile as an activator. The ratio of fabric to bath was 1:10.

The compositions of the baths per liter were as follows:

(a)

- 3.0 g. hydrogen peroxide 35%, 5 g. sodium perborate — Active oxygen containing substances.
- 1.5 g. water glass, .15 g. magnesium sulfate — Stabilizer.
- 0.3 g. N-phenylbiguanide — Protective agent.
- 1 g. iminodiacetonitrile — Activator.

(b)

- 3.0 g. hydrogen peroxide 35%, 5 g. sodium perborate — Active oxygen containing substances.
- 1.5 g. water glass, .1 g. magnesium sulfate — Stabilizer.
- 0.3 g. N-phenylbiguanide — Protective agent.

Both bleaches were carried out at 85° C. and with bath (a), a full white was achieved in 1 hour whereas, with bath (b), a full white was not achieved until after two hours.

The liberation of the oxygen and the bleach was accelerated by the presence of the activator, as can be seen from the following table:

Bath	Active oxygen content of bath after—		
	30 min.	45 min.	120 min.
	Percent	*Percent*	*Percent*
(a) With activator	69	61	52
(b) Without activator	99	95	94

The pH values of the baths were as follows:

(a) 9.4 at start and 9.1 at the end
(b) 9.6 at start and 9.3 at the end

The action of the fiber protective agent which was present in the bath was not diminished by the presence of the activator, as the loss in strength of the Perlon was only 5% despite a 2 hours' peroxide bleach.

Example 5

The nitriles according to the invention are also suited for the activation of finished packed powdered perborate washing compositions. While they promote the liberation of oxygen when the washing compositions containing them are dissolved in water they do not cause a decomposition of the perborate in the dry compositions.

The stability of the following dry washing powder compositions was observed over a period of ten months:

(a)

	G.
Soap shavings (85%)	150
Sodium pyrophosphate	40
Sodium perborate	10
Nitrilotriacetic acid nitrile	4
	204

On the day of production, such composition contained 0.55% of active oxygen and after 10 months' storage it still was 0.55%.

(b)

	G.
Soap shavings (85%)	150
Sodium pyrophosphate	40
Sodium perborate	10
Ethylene diaminotetraacetic acid nitrile	4
	204

The composition also as produced contained 0.55% of active oxygen and after 10 months' storage it was still 0.54%, so that the stability of the active oxygen in the dry state was not diminished to any substantial extent.

On the other hand, the cleavage of the active oxygen in aqueous wash baths at 65° C. was substantially accelerated, as can be clearly seen from the following table in which the active oxygen content of washing baths containing compositions (a) and (b) were compared with that of a bath (O) of the same composition but omitting the organic nitrile accelerator. In each instance, the bath originally contained 0.56 g./l. of active oxygen. Of course, the smaller the percentage of active oxygen remaining in the bath the greater the activation occurring.

Bath	Active oxygen content of bath after—		
	30 min.	60 min.	120 min.
	Percent	*Percent*	*Percent*
(O)	96	94	90
(a)	60	40	14
(b)	37	27	11

The pH values of the baths at the beginning of the tests were above 9.7 and at the end about 9.3. The acceleration of the oxygen liberation in the baths containing the accelerators intensified the bleaching action obtained considerably.

Example 6

A washing bath of the following composition per liter was prepared:

1.25 g. lauryl sulfate
0.625 g. sodium pyrophosphate
0.625 g. sodium tripolyphosphate
0.350 g. dry waterglass (53% SiO_2)
0.600 g. sodium perborate
0.200 g. terephthalic acid nitrile

and its active oxygen content compared with a bath of the same composition but with the omission of the terephthalic acid nitrile after 30, 60 and 120 minutes at 60° C.

Bath	Active oxygen content of bath after—		
	30 min.	60 min.	120 min.
	Percent	*Percent*	*Percent*
(a) without accelerator	99	98	96
(b) with accelerator	75	61	40

As can be seen from such table, the bath containing the nitrile liberated oxygen much more rapidly than the bath omitting such accelerator. The pH of the wash baths was 9.5.

Example 7

An aqueous wash bath of the following composition per liter was prepared:

5.70 g. Marseilles soap
1.50 g. calcined soda
0.75 g. sodium pyrophosphate
0.75 g. sodium tripolyphosphate
0.70 g. dry waterglass
0.60 g. sodium perborate
0.30 g. terephthalic acid dinitrile

This bath was used to wash a regenerated cellulose staple fiber textile fabric which had been soiled with blueberries at a fabric to bath ratio of 1:50 for 45 minutes at 60° C. In view of the accelerated oxygen liberation caused by the presence of the nitrile the same whitening effect was obtained as when the same textile fabric soiled with blueberries was washed for 45 minutes at 90° C. in a bath of the same composition but omitting the terephthalic acid dinitrile.

Example 8

A cotton fabric soiled with fruit juice was washed at 60° C. at a fabric-bath ratio of 1:20 for 2 hours in a bath which contained

10 g. Marseilles soap
2 g. sodium pyrophosphate
0.5 g. sodium perborate
0.3 g. phthalonitrile

per liter.

The whitening effect obtained was the same as with an analogously conducted boil wash in a bath omitting the nitrile activator.

Example 9

Work pieces of Bemberg silk (cuprammonium rayon) which had been soiled with tea were washed for 2 hours at 60° C. at a fabric to bath ratio of 1:25 in a bath containing

10 g. Marseilles soap
2 g. sodium pyrophosphate
0.5 g. sodium perborate
0.3 g. tetramethylene dinitrile

per liter.

The washing effect corresponded about to that obtained with a boil wash analogously conducted with a bath of the same condition but omitting the nitrile activator.

Example 10

A wash bath containing

10 g. Marseilles soap
2 g. sodium pyrophosphate
0.5 g. sodium perborate
0.2 g. methylene-bis-iminoacetonitrile

per liter was prepared and rayon staple fiber fabric soiled with red wine placed therein and treated therein for 45 minutes at 65° C. at a fabric to bath ratio of 1:50. The cleaning effect obtained was satisfactory. 56% of the active oxygen content of the bath was consumed during the treatment. On the other hand, in a bath of the same composition but omitting the methylene-bis-iminoacetonitrile only 6% of the active oxygen was consumed.

Example 11

Cotton nettle cloth which had been lightly soiled with chocolate milk was treated for 2 hours at 60° C. in an aqueous bath containing

5.70 g. Marseilles soap
1.50 g. calc. soda
0.75 g. sodium pyrophosphate
0.75 g. sodium tripolyphosphate
0.70 g. dry waterglass
0.60 g. sodium perborate
0.30 g. dimethyl-diamino-succinic acid dinitrile

per liter.

As a comparison, a portion of such soiled cloth was treated under the same conditions in a bath of the same composition but omitting the nitrile activator. The ratio of cloth to bath in both instances was 1:50.

The soil was removed to a much greater extent in the activated bath than in the unactivated bath.

Example 12

Swatches of fabric which were soiled with a copying pencil were treated at 60° C. with occasional movement in a washing and bleaching bath containing

10 g. Marseilles soap
2 g. sodium pyrophosphate
2 g. hydrogen peroxide (30%)
0.3 g. nitrilotriacetic acid nitrile

per liter. The ratio of fabric to bath was 1:50. A comparative test was carried out with the same bath but omitting the nitrilotriacetic acid nitrile under boil wash conditions. The degree of lightening of the fabric was the same in the bath containing the nitrilotriacetic acid nitrile at 60° C. as was obtained in the boil wash in the absence of such activator.

The active oxygen content of both baths was about the same, as can be seen from the following table:

Bath	Active oxygen content of bath after—		
	30 min.	60 min.	120 min.
	Percent	*Percent*	*Percent*
activated wash at 60° C.	58	48	39
unactivated boil wash	66	51	36

Example 13

Poplin which had been dyed with Sirius light blue GL, a dye which is sensitive to oxygen bleaching agents, was treated for 1½ hours at 60° C. with a washing bath

at a fabric to bath ratio of 1:50. The bath used contained

7.0 g. soap shavings
2.0 g. sodium pyrophosphate
1.0 g. sodium perborate
0.2 g. nitrilotriacetic acid nitrile

per liter.

It was found that the thus treated fabric lightened up as much as a fabric treated in the same bath but with the omission of the nitrilotriacetic acid nitrile under slow heating to the boiling point.

We claim:

1. In a process for the treatment of organic fibrous materials with an aqueous bath containing an inorganic peroxidic bleaching compound, the step which comprises carrying out such treatment in the presence of an organic nitrile compound possessing at least limited solubility in said bath.

2. The process of claim 1 in which the proportion of nitrile compound present is sufficient to provide about one nitrile group per mol of peroxidic oxygen.

3. The process of claim 1 in which said treatment is carried out at a temperature between 50 and 80° C.

4. The process of claim 1 in which said bath also contains a detergent.

5. The process of claim 1 in which said bath also contains a stabilizer for said peroxidic compound.

6. The process of claim 1 in which said bath also contains a protective agent for the fibrous material treated.

7. A bleaching composition comprising an inorganic peroxidic bleaching compound and an organic nitrile compound possessing at least limited solubility in water.

8. A dry bleaching composition comprising an inorganic peroxidic bleaching compound and an organic nitrile compound possessing at least limited solubility in water.

9. A dry bleaching and washing composition comprising a detergent, an inorganic peroxidic bleaching compound and an organic nitrile compound possessing at least limited solubility in water.

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