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(54) Detergent composition.

(57) Improved fabric washing detergent composition especially but not exclusively designed for washing mixed coloured fabrics comprising from 0.5 to 25% by weight of a peracid compound selected from the group consisting of organic peracids, peracid salts and peracid precursors which generate peracids by hydrolysis or perhydrolysis, and from 0.002 to 2.5% by weight of copper, in the absence or substantial absence of a powerful sequestrant which complexes strongly with copper. The composition is effective in minimizing dye transfer but is non-effective or substantially non-effective with respect to direct fabric dye or stain bleaching.

DETERGENT COMPOSITION

This invention relates to fabric-washing detergent compositions which are especially, but not exclusively, designed for the washing of coloured or mixed coloured and white fabric loadings.

Hitherto fabric-washing detergent compositions of two types were available, i.e. (1) washing products of a non-bleaching type for coloured fabrics, which, although safe for the fabric dyes themselves, are not effective to prevent the tendency of some coloured fabrics to release into the wash liquor dyes which are then transferred during the washing process onto other fabrics being washed therewith; and (2) a bleach-containing fabric-washing product type which can inhibit dye transfer to a certain extent but at the same time will cause bleaching and fading of the colours of the fabrics. Hence, heretofore there has been no good way to combat the problem of dye transfer other than by mechanically sorting the fabrics to partition fabrics with dark and light shades for separate laundering.

With the fashion of moving towards more coloured clothing and textile materials, especially multi-coloureds, the problem of dye transfer has become more acute. Many attempts have been made to resolve this problem, but so far without much success.

For example, in GB-A- 1 368 400 dye-transfer-inhibiting compositions were proposed which comprise a peroxygen compound, e.g. an organic peroxyacid, combined with rather complex aldehyde or ketone compounds as bleach activator. These compositions have several drawbacks in that not only do they use rather expensive complex organic chemical compounds, i.e. aldehydes and ketones, but also in that they are not very effective.

Other compositions having dye-transfer inhibitory effects are disclosed in European Patent 0024367 (based on the activation of organic peracids with bromide ions) and European Patent Application 0024368 (based on a system comprising an organic peracid precursor and a bromide activator). Still, the main drawback of these compositions is that they too exert a rather strong direct fabric bleaching, tending to cause fading of the coloured fabrics.

European Patent Application 0058444 describes washing compositions useful for the reduction of dye transfer in fabric washing at lower temperatures, comprising a bleach system consisting essentially of an organic peracid or an organic peracid precursor in conjunction with a water-soluble iodide salt. There are some snags in the use of iodide catalyst, i.e. 1) the risk of staining due to iodine formation and 2) the effect of direct fabric dye bleaching.

It is an object of the present invention to provide an improved fabric-washing detergent composition which is suitable for the washing of mixed coloured fabrics, including mixed loads of coloured and white fabrics, without the above drawbacks.

It is another object of the invention to provide a system that is effective for dye bleaching in solution, i.e. minimising dye transfer, but is non-effective or substantially non-effective with respect to direct fabric dye bleaching.

It has now been found that these and other objects which may be apparent hereinafter can be achieved by using a system comprising a peroxyacid and a copper catalyst in the absence or substantial absence of a powerful sequestrant which complexes strongly with copper.

Internal work has shown that transition metal ions can catalyse dye bleaching in solution by oxygen bleaches. So hydrogen peroxide or hydrogen peroxide adducts, inorganic persalt/bleach activator systems and peroxyacids per se can all be activated by copper ions. However, it has been found that copper-catalysed peracid bleach systems were much more effective than copper-catalysed hydrogen peroxide systems (e.g. sodium perborate).

The effect of added transition metal ions on the bleaching of a Direct dye in solution by peracetic acid was investigated under the following test conditions:

Conditions: Peracetic acid (4.6×10^{-4} moles/l) was added to a solution of Direct Red 81 (0.002% w/w) and the dye concentration measured at the wavelength of maximum absorption*. The experiments were repeated with added transition metal compounds ($CuSO_4$, $MnSO_4$, $CoCl_2$, $FeCl_3$, $NiSO_4$, $ZnSO_4$, $Ti(SO_4)_2$ as appropriate). The experiments were made at pH 9 and at 40°C.
The results are tabulated in Table I below :

* The λ max (490-510 nm) and maximum absorption (= 100% dye) were measured at the beginning of each experiment after the addition of transition metal compound but not before addition of bleach.

Table I

Added transition metal ion (1 ppm)	% dye remaining after 30 mins
-	97
Ti	97
Cr	95
Mn	83
Fe	80
Co	60
Cu	10
Zn	95

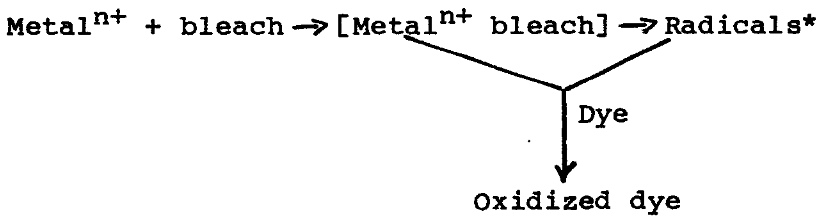
Mechanistically it is very important to recognise that transition-metal-catalysed dye bleaching has only been achieved with transition metal ions which are easily capable of one-electron redox processes leading to the formation of reactive radicals. However, as is shown in Table I, only copper and possibly cobalt gave catalysis of peracetic acid for dye bleaching, whereas all the other metals including chromium and zinc are inactive.

Without wishing to be bound to any theory, the mechanism of dye bleaching with oxidizing bleaches can be envisaged in general terms to progress via interactions of two distinct types:

Route A

$$\text{Metal}^{n+} + \text{dye} \rightarrow \text{Metal}^{n+}\ \text{dye} \xrightarrow[\text{(+ Bleach)}]{} \text{Dye Metal}^{n+}\ \text{bleach} \rightarrow \text{oxidized dye}$$

Route B



* The term "radical" is used herein in a very loose manner to describe species which can undergo one-electron reactions. The exact nature of the reactive radicals which undergo reactions with dye has not been determined.

It has also been found that although transition metal ions are well known to interact with peroxide compounds as in Route B above, thus inducing decomposition to radicals or radical species which are known to have high oxidation potential and are capable of oxidizing most unsaturated molecules, no other transition metals are as effective for dye transfer inhibition as copper.

A possible explanation therefor may be the less well known mechanism of transition metal ions to complex strongly with many dyes as in Route A above. This route to the interaction of transition metal with bleach, which is only after its interaction with dye, seems to be followed by copper. There seems also to be little doubt that, when it occurs, complexation of transition metal ion and dye will aid dye bleaching, because metal-catalysed bleach decomposition can thus take place in the vicinity of the dye via a dye-metal bleach complex. Thus the ease with which copper forms such complexes compared with other transition metal ions may be one reason why copper has proved to be generally the most useful transition metal ion for dye bleaching in solution. Cupric ion, being the smallest divalent transition metal ion, with the highest charge density, most readily forms stable complexes. Cobalt III and chromium III complexes of dyes are also very stable, but apparently they are kinetically inert and, in contrast to copper, severe conditions are generally necessary to introduce cobalt III and chromium III into dye structures.

In fact, copper is not the most powerful decomposer of bleach molecules. It is known that cobalt is much more effective in this respect, so the amount of free radicals or radical-like intermediates formed from oxygen bleaches is likely to be higher in the case of cobalt. The experimental observation that cobalt is less useful for bleaching dyes than copper may be attributed to the fact that for cobalt many of these radicals lead to useless bleach decomposition, whereas for copper they are more likely to be produced in the vicinity of the dye molecules.

Also manganese, which is known to be very useful for catalysing stain bleaching, especially with hydrogen peroxide bleaches in the presence of a carbonate, has proved to be ineffective for dye transfer inhibition. Experiments have even shown that under practical conditions manganese can inhibit the catalytic effect of copper, and so the presence of manganese ions in the system of the invention should preferably be avoided.

Some experiments have also been carried out by Applicants to determine whether strong metal-dye complexation is absolutely essential for good copper catalysis of dye bleaching in solution. From observations of the UV/visible spectra it is clear that CI Direct Red 81 and CI Acid Orange 7 dyes complex with copper. On adding copper sulphate to CI Acid Orange 52, an azo dye without orthohydroxy groups, there is, however, little change in the UV/visible spectrum, suggesting that the binding of this dye with copper is very weak. There is, however, a definite increase in the rate of dye bleaching when copper is added to a solution containing this dye and sodium monopersulphate (a peroxyacid salt) bleach, just as is obtained with the dyes which complex more strongly with copper.

Also when the complexation site of a bis ortho-ortho' dihydroxy azo dye was blocked with chromium, a metal which does not activate dye bleaching, as in CI Acid Blue 161, then, although there is no detectable change in the visible absorption spectrum on addition of copper to the dye alone, this addition in the presence of a monopersulphate bleach produces a considerable increase in the rate of dye bleaching. Thus these experiments indicated that copper complexation with dyes is not a necessary criterion for copper-catalysed dye bleaching and it must be concluded that, although the ability of copper to strongly complex with dyes under wash conditions plays a role in its generally found higher catalytic activity compared with other transition metal ions, copper catalysis still occurs even when the metal-dye complexation is weak or non-existent.

There is much evidence that copper-catalysed dye bleaching is intimately connected with the decomposition of bleach in solution. Increase in concentration of copper generally increases the rate of dye bleaching as well as the decomposition of bleach. Characteristically, it has been observed that the transition-metal-catalysed decomposition of a peroxide often exhibits an induction period which is reduced by higher levels of copper ions. Many experiments made with copper-catalysed dye bleaching similarly exhibit induction periods which are reduced by increasing the concentration of copper ions.

Thus, although this reduction in induction period is accompanied by an increased decomposition rate of bleach, acceleration of dye bleaching to avoid dye transfer can be effected by:

(a) increase in concentration of the bleach and copper (II) ions;

and furthermore by other means which increase the rate of radical production, viz :

(b) increase in the pH of the bleach liquor; and

(c) addition of a suitable reducing agent, e.g. hydrogen peroxide added as solid hydrogen peroxide adduct such as sodium perborate or percarbonate, which liberates hydrogen peroxide in solution.

The influence of cupric ion concentration on an experiment of dye transfer inhibition is shown in the following Table II for the peracid bleaches monopersulphate (Oxone®), diperisophthalic acid (Suprox®) and magnesium monoperphthalate, with and without sodium perborate.

The detergent base used in the experiments had the following composition :

Composition	Parts by weight
Sodium dodecylbenzene sulphonate	16.0
Coconut ethanolamide	3.0
Sodium toluene sulphonate	2.0
Sodium triphosphate	35.0
Anhydrous alkaline silicate	11.0
Sodium sulphate	10.6
Water	9.1

Table II

Influence of copper level on dye transfer inhibition due to peracid and peracid/perborate bleaches

Detergent base (4 g/l), 40°C, 30 min, CI yellow acid 64 dye transferring to cotton and nylon from nylon. Peracid (9.2×10^{-4} g atoms active oxygen per litre). Perborate (4.6×10^{-4} moles/litre, 0.0708 g/l). Copper as copper sulphate, 18° hard water.

	R425* Dye Transfer Monitors											
Copper level (ppm)	Monopersulphate Oxone (0.35 g/l)				Diperisophthalic acid Suprox (0.399 g/l)				Monoperphthalate (0.284 g/l)			
	Cotton		Nylon		Cotton		Nylon		Cotton		Nylon	
	- Perb	+ Perb	- Perb	+ Perb	- Perb	+ Perb	- Perb	+ Perb	- Perb	+ Perb	- Perb	+ Perb
0	52.9	57.2	70.0	73.2	51.0	52.4	66.0	67.6	50.9	50.1	69.0	67.0
0.1	54.3	63.0	70.7	77.2	51.5	59.1	67.2	73.2	51.6	53.9	69.5	70.6
0.6	54.3	74.6	71.7	82.8	53.1	66.4	68.3	79.0	52.2	61.0	70.3	76.5
2.0	58.2	73.3	73.5	82.0	57.5	70.6	72.2	80.9	54.4	65.0	72.1	79.2
4.0	60.9	74.4	76.3	82.5	61.1	71.8	74.4	81.5	54.6	66.6	72.5	80.4
8.0	62.7	75.1	75.4	82.4	64.6	72.1	77.0	81.2	56.6	67.2	74.1	79.7
16.0	66.2	74.2	81.2	84.6	69.5	73.1	80.9	82.6				
32.0	69.6	74.4	82.1	85.2	73.4	73.6	81.7	82.7				
64.0	72.0	76.1	81.4	84.6	75.9	75.7	82.3	82.8				

* R 425 = Reflectance measured at λ max. (425 nm), i.e. wave length of maximum absorption.

The influence of pH on dye transfer inhibition with copper-catalysed monopersulphate bleach systems is shown in Table III.

The influence of increasing pH on the rate of copper-catalysed bleaching of Direct Red 81 with various per-acids, i.e. I (diperisophthalic acid), II (monopersulphate) and III (peracetic acid) is shown in Fig. 1.

The dye concentration in g/l (vertical axis) was set out against pH (horizontal axis) under the following experimental conditions :

Direct Red 81 (0.002 g/l), peracid (4.6×10^{-4} g. atoms of active oxygen), pH stat. at 40°C.
The diperisophthalic acid used was a commercial product "Suprox"; monopersulphate used was a commercial product "Oxone"; and the peracetic acid used was pretreated with catalase to remove H_2O_2.

It can be seen from this figure that overall there is a considerable increase in dye bleaching with increasing pH.

Table III

Influence of pH on dye transfer inhibition with copper-catalysed monopersulphate bleach systems

Wash conditions: 40°C, 18° hard water, 30 min, Detergent base 4 g/l 18° hard water.
Monopersulphate 9.2 x 10^{-4} moles/litre. Copper (4 ppm as $CuSO_4.5H_2O$).
Perborate 4.6 x 10^{-4} moles/l. CI Acid 64 Dye transferring to cotton and nylon.

	R425*							
	Cotton Dye Transfer				Nylon Dye Transfer			
pH	Base Alone	Monopersulphate	Monopersulphate + perborate	Perborate	Base Alone	Monopersulphate	Monopersulphate + perborate	Perborate
6	63.3	64.4	65.5	65.2	58.1	60.2	60.5	60.0
7	59.0	64.2	65.6	61.3	56.4	63.7	64.3	57.8
8	55.8	63.9	70.9	58.5	57.8	66.1	74.3	58.0
9	51.0	62.9	74.2	54.4	62.5	72.5	81.4	61.9
10	48.3	62.9	73.5	51.3	69.2	78.9	82.7	68.4
11	48.5	62.9	62.6	51.1	72.8	82.0	81.4	74.1

* Reflectance measured at λ max. (425 nm), i.e. wave length of maximum absorption.

The above Tables II and III also show the influence of adding perborate (sodium perborate) to monopersulphate, diperisophthalic acid or magnesium monoperphthalate on the dye-transfer problem.

It can be seen that, in general, the addition of perborate gave a considerable enhancement of the dye transfer reduction. A molar ratio of peracid : perborate of about 2:1 was found to be the optimum. Higher levels of perborate will tend to a reduced enhancement and sometimes even a reduced effect.

The dye bleaching in solution and tergotometer dye transfer experiments were carried out by the following methods:

Bleaching dyes in solution

Apparatus

The apparatus consists of a Beckman DB spectrophotometer fitted with a 1 cm silica flow cell, a water bath to maintain the temperature of the bulk liquor and a pH stat to control the pH. The cell is connected to the solution with small-bore silicon rubber tubing and the liquor is circulated by a Watson Marlow flow inducer. This is fitted on the return tube from the cell to the bulk solution to prevent accidental flooding of the cell compartment. The silicon rubber tubes enter the cell compartment of the spectrophotometer through small holes in the lid. The small amount of light which must enter here does not affect readings in the visible range.

The Flow Cell

The silica flow cell has a path length of 1 cm. Its stopper has a glass entry tube almost reaching the bottom of the cell and set to one side out of the light path. A short exit tube takes the solution from the top of the cell through the pump and back to the bulk solution.

Method

A 0.04% w/v stock solution of dye was diluted with demineralised water to give 250 ml of 0.004% solution. This was poured into a 600 ml beaker set in the water bath preheated to 40°C and the pH was adjusted. The solution was then pumped through the cell at a rate of 40 ml per minute. This gives a good flow through the cell without turbulence causing bubbles. The per cent transmission at max for the dye was monitored on the recorder.

A further 250 ml of demineralised water containing 1.137×10^{-4} m of peracid was warmed to 40°C and the pH adjusted. This was added to the dye solution and the change in % transmission was recorded for one hour. During this time, the solution was stirred constantly and, at various time intervals, 50 ml aliquots were taken for titration with M/200 sodium thiosulphate.

When reagents such as electrolytes, surfactants or bleaching aids were to be used, they were added as the first dye solution was prepared.

Bleaches were compared at equal active oxygen concentrations.

Calculation of Dye Concentration

The dye solution was scanned from 700 nm to 400 nm to find the maximum absorption wavelength. Then an absorption (at λ max) vs concentration (% w/v) graph was plotted and the slope calculated.

The dye solutions were recorded as the change in % transmission. Therefore, the concentration of dye present at any time was calculated as:

$$\text{Concentration of dye (\% w/v)} = \frac{2 - \log \% T}{\text{slope}}$$

Slope = the slope of the absorption vs concentration graph.

Dye Transfer Experiments - Test Method

The Dyed Test Fabrics

Test fabrics with different dye types are used. One 17.5 cm x 17.5 cm square of dyed test cloth was used in each wash.

The Dye Transfer Monitors

The fabrics for dye pick-up were white mercerised, de-sized cotton shirting and white bulked nylon 66, both non-fluorescent. One 12 cm x 12 cm square of each of these was put into the wash, regardless of the dye type, to keep the liquor to cloth ratio the same.

Wash Conditions

The sets of test cloths were washed in the Terg-O-Tometer for 30 minutes at a constant 40°C and 100 rpm. The product concentration was 0.4% w/v in 18° hard water with a liquor to cloth ratio of 50:1. Each set of cloths was rinsed separately with three 600 ml portions of cold 18° hard water.

Wash Method

450 ml portions of 18° hard water were poured into the Tergo pots and allowed to warm up to 40°C. The pre-weighed constituents were then added. One dyed test fabric and one each of the clean cotton and nylon test cloths were added and washed for 30 min. at 100 rpm.

At the end of the wash, the sets of cloths from each pot were put into separate 600 ml portions of cold 18° hard water. The rinses were then continued, each set of cloths being rinsed three times in 600 ml portions of cold 18° hard water.

After rinsing, the cloths were separated, padded on paper towelling to remove excess moisture and dried in a cabinet at 60°C.

Measurement of Dye Pick-up

The reflectance of the cloths was measured at the maximum absorbence wavelength of the dye using a Beckmann DB-GD grating spectrophotometer fitted with a diffuse reflectance attachment. Barium sulphate was used to standardise the instrument and as a reference when measuring the cloths.

From the above experimental results it can be said that the composition of the invention should preferably contain at least 0.002% by weight of copper, i.e. equivalent to about 0.1 ppm in solution, should preferably have a 5 g/l solution pH of from about 7 to about 11, and should preferably contain a hydrogen peroxide adduct at molar ratios to peracid which can be as low as about 1:100 up to about 2:1, most preferably from 1:25 to 1:1.

For practical reasons, the upper limit of the copper concentration can be set at about 2.5% by weight based on the total composition.

As the source of copper, any copper salt can be used in the practice of the invention, for example copper sulphate, copper carbonate, copper chloride, copper phosphate etc.

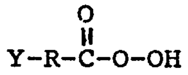
As already elucidated before, sequestration of copper by strong sequestrants should be minimized so as to favour dye/copper interaction and the production of radicals from the bleach, but on the other hand excessive bleach decomposition must be avoided during storage of the powder. Hence the presence of very minor amounts of a relatively weak sequestrant such as ethylene diamine tetra-acetates (EDTA) can be tolerated in the present invention at levels usually below 0.2% by weight, preferably up to about 0.1% by weight, based on the total composition. The level of sequestrant tolerated will depend on the level of copper added.

In practice, where the invention is used in a normal phosphate-built detergent composition, a higher level of copper in the formulation is required. Hence a preferred level of copper in such formulations will in general be at least about 0.02% by weight.

From theoretical considerations, stain chromophores on fabrics, which are generally quinonoid in character, are unlikely to behave very differently to dyes in bleaching reactions. Dyes of different types, e.g. azo, quinonoid and indigoid, have all been found to respond to transition metal ion catalysis in solution. However, whereas dyes can be bleached in solution (i.e. a homogeneous reaction), in order to bleach dye on the cloth, the bleach must transfer from the solution phase into (or onto) the substrate phase. A surprising feature of the present invention is that generally no positive catalysis of dye or stain bleaching on the fabric is observed from copper added to the wash solution. The effect of copper in solution is likely to deplete the concentration of transferable bleach species (bleach anion ROO^- and especially undissociated ROOH) in solution and thus to reduce the amount of bleach available to undergo phase transition into the dye or stain on the fabric, thus reducing direct fabric bleaching.

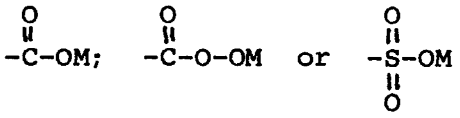
It should be appreciated that the invention as described hereinbefore for peracids is also applicable to peracid precursor systems which form organic peracids in aqueous media by hydrolysis or perhydrolysis.

The organic peracids which can be used in the present invention are known in the art. They can be either aliphatic or aromatic and have the general formula:



$$Y\text{-}R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}OH$$

wherein R is an alkylene group containing from 1-16 carbon atoms or an arylene group containing from 6-8 carbon atoms and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution, for example:



$$\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OM; \quad \text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}OM \quad \text{or} \quad \text{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\text{-}OM$$

wherein M is hydrogen or a water-soluble salt-forming cation.

Examples of aliphatic peracids are peracetic acid, monoperazelaic acid, diperazalaic acid, diperadipic acid, diperoxy dodecanoic acid and decyl butane diperoxoic acid.

Examples of aromatic peracids are monoperoxy phthalic acid, perbenzoic acid, m-chloro-perbenzoic acid, diperisophthalic acid or mixtures thereof.

Examples of peracid salts as meant here include magnesium monoperphthalate, potassium monopersulphate, and peroxymonophosphate. Mixtures of peracids (with or without a hydrogen peroxide adduct) may be useful in practice.

In systems where the peracid is formed *in situ* from its precursor or precursors, the peracid can be formed from the combination of an organic peracid precursor, so-called "persalt activator" and a persalt of the peroxyhydrate type, e.g. sodium perborate, by perhydrolysis, or from a precursor which generates peracid by hydrolysis. Hence various peracid precursors will fall within the scope of use in the compositions of the invention. These include benzoyl peroxide and diphthaloyl peroxide, both of which are capable of generating peracids, i.e. perbenzoic acid and monoperoxyphthalic acid, respectively.

Precursors which generate peracid on perhydrolysis are known in the art and include esters, such as those described in British Patents 836,988 and 970,950, including glycerol penta-acetate and tetra-acetyl xylose; acyl amides, such as N,N,N',N'-tetra-acetyl ethylene diamine (TAED), tetra-acetyl glycoluril, N,N'-diacetyl acetoxy methyl malonamide and others described in British Patents 907,356; 855,735; 1,246,339 and US Patent 4,128,494; acyl azoles, such as those described in Canadian Patent 844,481; acyl imides, such as those described in South African Patent 68/6344; and triacyl cyanurates, such as described in US Patent 3,332,882.

The amount of peracid compound in the composition of the invention will be in the range generally of from 0.5 to 25% by weight, preferably from 1 to 15% by weight.

These levels as defined for peracid compounds are applicable to organic peracids, peracid salts as well as precursors which generate peracids by hydrolysis or perhydrolysis.

In systems comprising an organic peracid precursor and a persalt, the organic peracid precursor will advantageously be used in stoichiometric ratio to the persalt, though higher ratios of persalt to organic precursors can also be used, particularly if a persalt bleach scavenger, such as catalase, is present. Preferred persalts are sodium perborate and sodium percarbonate.

Precursors which generate peracids on perhydrolysis are therefore usable at levels of about 0.5-25% by weight, preferably 1-15% by weight, in conjunction with a persalt at levels of about 0.5-50% by weight, preferably 0.5-30% by weight of the composition.

The invention therefore provides an improved fabric-washing composition especially but not exclusively designed for the washing of mixed coloured fabrics, comprising from 0.5 to 25% by weight of a peracid or a peracid precursor as hereinbefore defined and at least 0.002% by weight of a copper cation in the absence or substantial absence of a powerful sequestrant which complexes strongly with copper.

Preferably the washing composition of the instant invention contains a surfactant. The surfactant can be anionic, nonionic, cationic, semi-polar, ampholytic or zwitterionic in nature, or can be mixtures thereof. Anionics/nonionics and cationics/nonionics are typical basic surfactant mixtures. These surfactants can be used at levels from about 5% to about 50% of the composition by weight, preferably at levels of about 10% to 35% by weight.

Typical anionic non-soap surfactants are the alkylbenzene sulphonates having from 8-16 carbon atoms in the alkyl group, e.g. sodium dodecyl benzene sulphonate; the aliphatic sulphonates, e.g. C_8-C_{18} alkane sulphonates; the olefin sulphonates having from 10-20 carbon atoms, obtained by reacting an alpha-olefin with gaseous diluted sulphur trioxide and hydrolysing the resulting product; the alkyl sulphates, such as tallow alcohol sulphate; and further the sulphation products of ethoxylated and/or propoxylated fatty alcohols, alkyl phenols with 8-15 carbon atoms in the alkyl group, and fatty acid amides having 1-8 moles of ethylene oxide or propylene oxide groups. Other anionic surfactants usable in the present invention are the alkali metal soaps (e.g. of C_8-C_{22} fatty acids).

Typical nonionic surfactants are the condensation products of alkyl phenols having 5-15 carbon atoms in the alkyl group with ethylene oxide, e.g. the reaction product of nonyl phenol with 6-30 ethylene oxide units; the condensation products of higher fatty alcohols, such as tridecyl alcohol and secondary C_{10}-C_{15} alcohols, with ethylene oxide, known under the trade-name of "Tergitols"®, supplied by Union Carbide; the condensation products of fatty acid amine with 8-15 ethylene oxide units and the condensation products of polypropylene glycol with ethylene oxide.

Typical cationic surfactants include the conventional quaternary ammonium compounds and the C_{10}-C_{25} alkyl imidazolinium salts. Preferred quaternary ammonium compounds are the di(C_{16}-C_{20} alkyl)di(C_1-C_4 alkyl) ammonium salts such as ditallow dimethyl ammonium chloride; ditallow dimethyl ammonium methylsulphate; dihydrogenated tallow dimethyl ammonium chloride or methyl sulphate; dioctadecyl dimethyl ammonium chloride; dicoconut alkyl dimethyl ammonium chloride. Also suitable are the single long chained quaternary ammonium compounds wherein the long chain is a C_{10}-C_{22} alkyl or alkenyl group.

A preferred member of the class of C_{10}-C_{25} alkyl imidazolinium salts, believed to be the 1-methyl-2-tallow-3-(2-tallow amide ethyl) imidazolinium chloride, is sold under the trade-name of Varisoft 455 or 457 (Ashland Chemical Company) or Stemoquat M 5040/H (Chemische Werke Rewo).

A typical listing of the classes and species of surfactants useful in this invention appears in the books "Surface Active Agents", Vol. I, by Schwartz & Perry (Interscience Publishers 1949) and "Surface Active Agents and Detergents", Vol II, by Schwartz, Perry & Berch (Interscience 1958), the disclosures of which are incorporated herein by reference.

Generally, a washing composition of the invention will also include one or more detergency builders and alkaline materials. Usually the total amount of detergency builders in a detergent composition of the invention will be from about 5 to about 70% by weight of the detergent composition. Many detergency builders are known, and those skilled in the art of formulating fabric-washing detergent compositions will be familiar with these materials. Examples of known detergency builders are sodium triphosphate; sodium orthophosphate; sodium pyrophosphate; sodium trimetaphosphate; sodium carbonate; sodium silicate; sodium oxydiacetate; sodium salts of long-chain dicarboxylic acids, for instance straight-chain (C_{10} to C_{20}) succinic acids and malonic acids; sodium salts of alpha-sulphonated long-chain monocarboxylic acids; sodium salts of polycarboxylic acids, i.e. acids derived from the (co)polymerisation of unsaturated carboxylic acids and unsaturated carboxy acid anhydrides, such as maleic acid, acrylic acid, itaconic acid, methacrylic acid, crotonic acid and aconitic acid, and the anhydrides of these acids, and also from the copolymerisation of the above acids and anhydrides with minor amounts of other monomers, such as vinyl chloride, vinyl acetate, methyl methacrylate, methyl acrylate and styrene; and modified starches such as starches oxidized, for example using sodium hypochlorite, in which some anhydroglucose units have been opened to give dicarboxyl units. Another class of suitable builders is the insoluble aluminosilicates as described in British Patents 1 429 143, 1 470 250 and 1 529 454, e.g. zeolite A.

Further, a detergent composition of the invention may contain any of the conventional detergent composition ingredients in any of the amounts in which such conventional ingredients are usually employed therein. Examples of these additional ingredients are lather boosters, such as coconut mono-ethanolamide and palmkernel mono-ethanolamide; lather controllers, inorganic salts, such as sodium sulphate and magnesium sulphate; anti-redeposition agents, such as sodium carboxymethylcellulose; and, usually present only in minor amounts, perfumes, colorants, fluorescers, corrosion inhibitors and germicides.

The washing composition of the present invention can suitably be used in relatively short washes as well as in relatively longer soak-washings under room temperature conditions up to 60°C for coloured fabrics, with a minimal risk of dye transfer and without the risk of serious direct fabric bleaching.

It should be appreciated that the invention can also be formulated as a washing or bleach adjunct to improve the performance of existing detergent compositions, e.g. fine wash products. In that case the system will essentially consist of a dry mixture of 0.5 to 25 parts by weight of a peracid compound and 0.002 to 2.5 parts by weight of a copper catalyst, e.g. cupric sulphate or cupric chloride, and optionally an inert filler such as sodium sulphate.

The washing compositions of the invention are preferably particulate, either as flowable powders or aggregates.

They can be prepared using any of the conventional manufacturing techniques commonly used or proposed for the preparation of particulate detergent compositions, such as dry-mixing, or slurry-making followed by spray-drying or spray-cooling and subsequent dry-dosing of sensitive ingredients, e.g. the solid organic peroxyacid compound, the peroxyacid precursor and the inorganic peroxyhydrate salt.

Other conventional techniques for taking precautions to improve storage stability or to minimize undue and undesirable interactions during storage between the bleaching agents and copper or other components of the detergent compositions, such as noodling, granulation, pelletizing and coating of any of the compounds may be utilized as and when necessary.

CLAIMS

1. Fabric washing detergent composition especially but not exclusively but not exclusively designed for washing mixed coloured fabrics, comprising from 0.5 to 25% by weight of a peracid compound selected from the group of organic peracids, peracid salts and peracid precursors which generate peracids by hydrolysis or perhydrolysis, and from 0.002% to 2.5% by weight of copper in the absence or substantial absence of a powerful sequestrant which complexes strongly with copper.

2. Detergent composition according to Claim 1, characterized in that the composition has a solution pH (5 g/l) of from 7 to 11.

3. Detergent composition according to Claim 1 or 2, characterized in that said peracid compound is selected from organic peracids and peracid salts.

4. Detergent composition according to Claim 3, characterized in that it further comprises a hydrogen peroxide adduct in a molar ratio of peracid compound : hydrogen peroxide adduct of from 100:1 to 1:2.

5. Detergent composition according to Claim 4, characterized in that said molar ratio is from 25:1 to 1:1.

6. Detergent composition according to Claim 5, characterized in that said molar ratio is 2:1

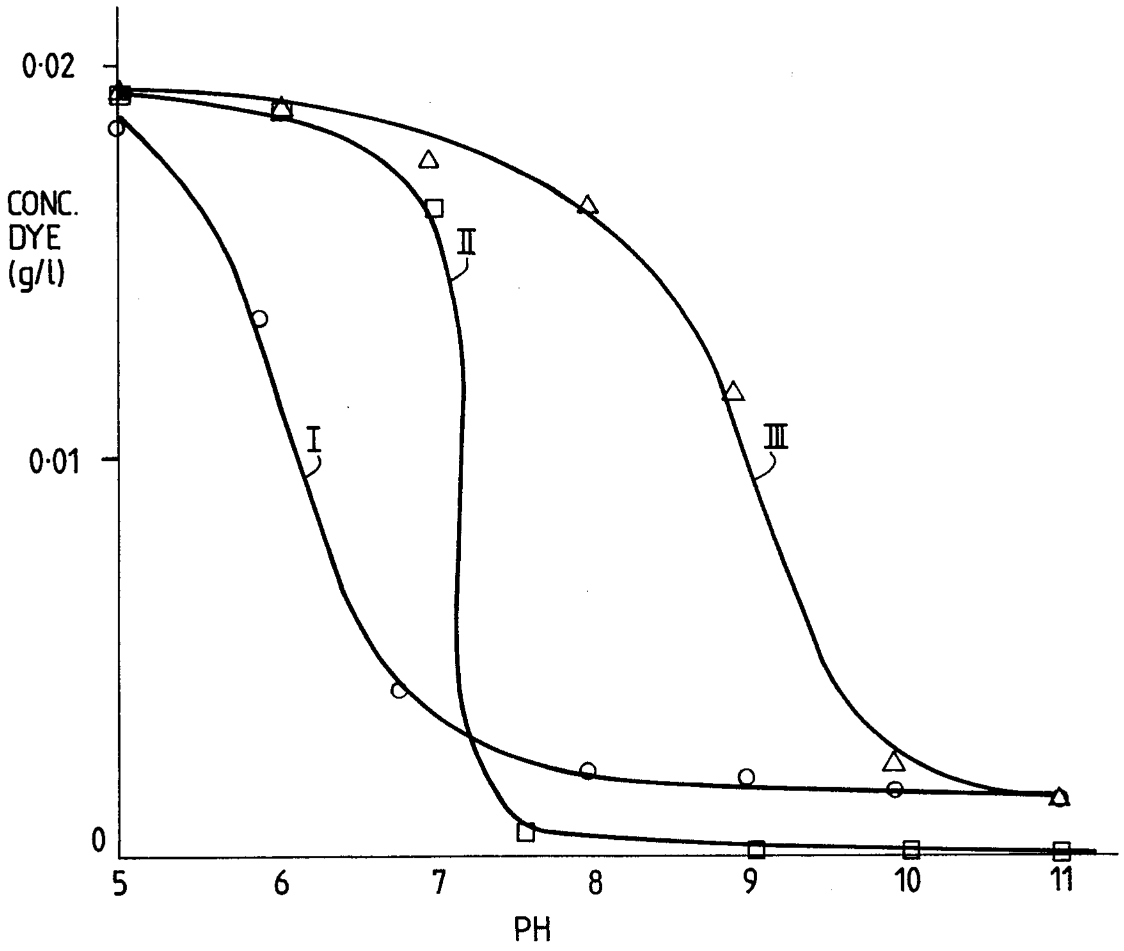
7. Detergent composition according to Claim 1 or 2, characterized in that it comprises 0.5-25% by weight of a peracid precursor which generates peracids by perhydrolysis and 0.5-50% by weight of a persalt.

8. Detergent composition according to any one of the above Claims, characterized in that it further comprises a surfactant selected from the group of anionic, cationic, nonionic, semi-polar, ampholytic and zwitterionic surfactants and mixtures thereof in an amount of from 5 to 50% by weight of the total composition.

9. Detergent composition according to any one of the above Claims, characterized in that it further comprises from 5 to 70% by weight of a detergency builder.

10. Detergent composition according to Claim 9, characterized in that said detergent builder is a phosphate builder.

11. Detergent composition according to Claim 9 or 10, characterized in that it comprises from 0.02-2.5% by weight of copper.


0·02
0·01
0
CONC.
DYE
(g/l)
I
II
III
5
6
7
8
9
10
11
PH