

PATENT SPECIFICATION

(11) 1 568 358

1 568 358

(21) Application No. 47372/75 (22) Filed 18 Nov. 1975
 (23) Complete Specification filed 25 Oct. 1976
 (44) Complete Specification published 29 May 1980
 (51) INT CL³ C07C 179/10; D06L 3/02
 (52) Index at acceptance
 C2C 220 227 22Y 30Y 351 354 356 541 544 547 645 665 69Y
 80X AA YR
 D1P 1200 1202 1204 1208 1211 1281 1303 1307 1308 1317 DS
 (72) Inventors JOSEPH EDMUND McCRUDDEN and ALAN SMITH

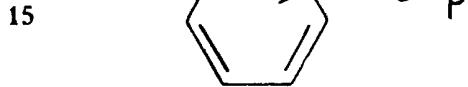


(54) AROMATIC PEROXYACIDS AND THEIR USE IN
 BLEACHING PROCESSES

(71) We, INTEROX CHEMICALS LIMITED, a British Company of Hanover House, 14 Hanover Square, London W1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

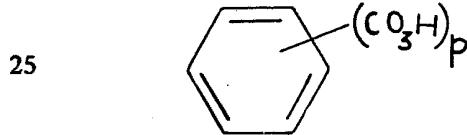
10 The present invention relates to peroxyacids, a method of preparing peroxyacids and processes for bleaching.

According to the present invention there is provided a peroxyacid having the general formula I:—



wherein p=3, or 4 or salts thereof, the benzene nucleus being optionally substituted by an alkyl, chloro or nitro group.

20 According to a second aspect of the present invention there is provided a process for bleaching textile materials, hard surfaces, wood and pulp with an aqueous solution of a peroxyacid having the general formula I:—



where p=3 or 4 or salts thereof, the benzene nucleus being optionally substituted by an alkyl, chloro or nitro group. As the number of peroxycarboxy groups substituted in the benzene ring increases, we have found that the stability of the compound tends to decrease. In consequence, the peroxyacids according to the pre-

sent invention contain no more than 4 peroxyacid groups.

One use of the peroxy acids described herein is in removing stains from textile fabrics. We have found that aromatic peroxyacids containing at least three peroxyacid groups tend to be more effective stain removers in alkaline solution than the corresponding peroxyacids which contain carboxy groups in that, at any given available oxygen concentration, the carboxy-free compound tends to effect a higher % stain removal than the corresponding carboxy-containing compound. Although we do not wish to be bound by any theory, we believe that this phenomenon may be caused by electrostatic repulsion between the bleaching species and the negatively charged fabric surface. Carboxy groups have in general a much lower pKa than peroxy-carboxy groups, and hence at any given pH a higher proportion of carboxy groups will be ionised than is the case for the corresponding peroxy-carboxy groups. Thus, the tendency of the molecule to be negatively charged increases as the proportion of carboxy groups increases, and hence the degree of repulsion between bleaching species and cloth increases.

Suitable peroxyacids include 1,2,4-triperoxytrimellitic acid, 1,3,5-triperoxytrimesic acid, 1,2,3-triperoxyhemimellitic acid, 1,2,4,5-tetraperoxytrimesic acid and 1,2,3,4-tetraperoxytrimesic acid.

Herein a reference to "organic peroxides" is to an organic peroxyacid containing three or four peroxyacid groups, or to the corresponding compound containing an acyl peroxide group from which the full peroxyacid is generated by perhydrolysis.

The organic peroxide described herein is preferably in contact with a desensitising amount of a desensitising diluent, i.e. an amount which reduces the impact sensitivity sufficiently to render the composition non-hazardous. In a standard drop weight test, 30 mg of material, which has been sieved to finer than 710

35

40

45

50

55

60

65

70

75

microns, is placed on an anvil in the apparatus. The anvil is centred and the sample tamped lightly by a force of 5 Kg-cm. A weight is then dropped several times from a given height, each time onto a fresh sample, and its effect observed. A positive result can range from being merely a discoloured product, through emission of a cloud of smoke, to, in an extreme case, an explosion. Tests are carried out at a series of heights. A higher proportion of positive results occur when a greater force is employed. The figure usually quoted is the median point, i.e. the point at which 50% of the results at a given force are positive. Compositions having a median point of at least 200 kg. cm are considered to be non-hazardous, but to provide a greater margin of safety compositions preferably have a median point of at least 300 kg.cm. Generally the amount is within the range 0.5 to 10 parts by weight of diluent per part of organic peroxide. Suitably the desensitising diluent can be selected from hydrocarbons having melting points in excess of 30° C., e.g. microcrystalline waxes, aliphatic fatty acids e.g. lauric and stearic acids, aromatic acids e.g. benzoic acid, alkyl e.g. t-butyl esters of the aliphatic or aromatic acids, protein or starch materials, boric acid and especially alkali and alkaline earth metal salts or halogen-free acids having a first dissociation constant of at least 1×10^{-3} e.g. sodium sulphate, magnesium sulphate and sodium tripolyphosphate. The intimate contact can be by way of admixing particles of the diluent with the organic peroxide or by granulating or coating the organic peroxide with the diluent. More than one diluent may be employed, conveniently first contacting the organic peroxide with an unreactive diluent described hereinbefore, and then coating the mixture with a second diluent. Such second diluent can be selected from fatty acid alkanol-amides, fatty alcohol polyglycol ethers, polyglycol/polypropylene oxide polymers alkaryl polyglycol ethers, polyethylene glycol and fatty acid esters and, amides thereof, and esters and amides of glycerol and sorbitol, polyvinyl alcohol, polymethyl methacrylate, dextrin, starch, gelatin carboxymethyl methacrylate, solid hydrocarbons, aliphatic fatty acids, fatty alcohols, sodium sulphate and magnesium sulphate. "Fatty", in the terms "fatty alcohol" and "fatty acid", is used to denote at least 12, desirably from 12 to 26 carbon atoms in the longest chain. Normally the amount of coating is within the range of 3% to 35% by weight based on the weight of the coated product. An organic peroxide thus coated is less prone to decomposition when stored in contact with alkaline surfactants, such as sodium salts of alkyl benzene sulphonates, which are commonly employed in detergent and bleaching compositions.

Detergent or bleaching compositions containing the organic peroxide also contain a surfactant and a builder salt, often contain a processing additive and detergent adjuncts such as organic sequestrants e.g. EDTA, peroxy-acid stabiliser (i.e. bleach stabiliser) e.g. dipicolinic acid, anti-redeposition agents, perfumes, colouring materials, optical brightening agents and inorganic active oxygen-containing compounds, hereinafter called persalts, which generate perhydroxyl ions in aqueous solution, such as sodium perborate tetrahydrate or monohydrate or sodium percarbonate (the commercially available hydrogen peroxide addition product) enzymes, dedusting agents, tarnish inhibitors and abrasives. If desired, the persalt together with some other diluent can be granulated with the organic peroxide.

Suitable builder salts can be either organic, for example, aminopolycarboxylates, organic polyphosphates, sodium citrate or sodium gluconate, or inorganic, for example, alkali metal carbonates, silicates, phosphates, polyphosphates or aluminosilicates. Typically, builders are present in proportions of from 1% to 90% by weight. Such compounds alter the pH detergent/bleaching solutions. Preferably sufficient builder salt is used to obtain a solution having a pH in the range of from pH 7 to 11, more preferably from pH 8 to 11.

A typical processing aid is sodium or magnesium sulphate which is conveniently incorporated in detergent or bleaching compositions in an amount of from 1 to 40% by weight.

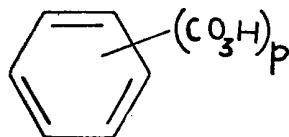
Where some builder salt or processing aid has been used to desensitise the organic peroxide the amount so used is included in the total amount of builder salt or processing aid present in the composition.

The surfactants may conventionally be water-soluble anionic, non-ionic, amphoteric or zwitterionic surface active agents. Suitable surfactants are often selected from acids and their alkali metal salts, alkyl sulphonates, alkylated aryl sulphonates, especially linear alkyl benzene sulphonates, sulphated aliphatic olefins, sulphated condensation products of aliphatic amides and quaternary ammonium compounds. The surfactants are normally present in the detergent composition in amounts of from 1% to 90% by weight, often in a weight ratio to the builder salts of from 2:1 to 1:10.

The bleaching composition can include any compound or compounds which enhance the bleaching or washing activity or organic peroxyacids, such as ketones and aldehydes as described in U.S. Patent No. 3822114 or certain quaternary ammonium salts as described in British Patent 1378671, both to Procter and Gamble. Some compositions comprising diacyl peroxides suitable for mixing with bleaching or detergent compositions are also described and claimed in our British Patent No. 1538744.

One convenient method of providing a desensitised composition suitable for incorporation in a detergent composition and substantially isolated from alkaline surfactants is to form a mixture of particulate organic peroxide with a particulate inorganic diluent such as sodium sulphate or tripolyphosphate or magnesium sulphate into tablets or extrudates. Such tablets or extrudates by themselves effectively reduce the surface of organic peroxide presented to the alkaline surfactants, and thus alleviate the problem of loss of active oxygen during storage. The problem can be further alleviated by providing an outer layer around the tablets or extrudates comprising at least one of the compounds described in the immediately preceding paragraph, generally in an amount of up to 20% by weight. Alternatively any suitable organic compound described herein before may be formed into a sachet within which a desensitised composition can be placed.

According to a third aspect of the present invention there is provided a method of preparing a peroxyacid having the general formula I



wherein p=3 or 4

the benzene nucleus being optionally substituted by an alkyl, chloro or nitro group comprising the step of reacting an aromatic carboxylic acid having its acid groups located around the benzene nucleus at the positions in which it is desired to obtain peroxycarboxylic acid groups, with hydrogen peroxide in a non-aqueous polar solvent, provided that where the aromatic carboxylic acid contained two acid groups in ortho relationship an internal acyl peroxide is formed in the aforementioned step instead of two peroxyacid groups, and in a subsequent step, the peroxy acid having the general formula I is generated in aqueous solution by perhydrolysis of the acyl peroxide. Thus oxidation of trimesic acid in methane sulphonic acid a non aqueous polar solvent at approximately 30° C., with excess hydrogen peroxide produces triperoxytrimesic acid, but under similar conditions oxidation of pyromellitic acid produces a compound believed to contain two intra acyl peroxide linkages, which is perhydrolysed in aqueous solution to produce tetra peroxy-pyromellitic acid. In view of the inclusion of several atoms of oxygen per molecule it is advised that great care be taken in the preparation.

Where the molecule contains an intramolecular acyl peroxide linkage as in the case of the oxidation product from pyromellitic acid, where two acid groups are in ortho rela-

tionship, the step of perhydrolysis is essential in order to generate the peracid. It is preferable to use intra acyl peroxide in the aqueous solution in conjunction with and the bleaching composition contain, at least one of the acid persalts, preferably in a ratio of from 1:2 to 2:1 molecules of persalt per acyl peroxide linkage, and advantageously 1:1.

Generally, bleaching solutions containing the organic peroxide contain at least 1 ppm available oxygen "av. ox" and for use in washing textile fabrics e.g. cotton or polyesters, often from 5 to 200 ppm. Solutions for cleaning hard surfaces such as metal, plastic or wooden surfaces can contain from 200 ppm to 500 ppm "av. ox". Peroxyacid solutions described herein can be used to bleach textile fabrics, wood and pulp under the conditions, and employing the equipment, used for bleaching with hydrogen peroxide or inorganic peroxyacids.

Suitably, bleaching with the compositions described herein can take place at an ambient temperature or higher, often from 20° C. and conveniently from 25° C. to about 60° C. In general the bleaching is effected at a controlled pH of about 8.5 to 11.5. Suitably the solutions can be produced by dissolving appropriate amounts of the detergent or bleaching compositions described hereinbefore.

Specific embodiments of the present invention will now be described more fully by way of example.

Example 1.

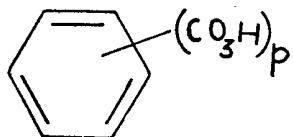
The effectiveness of bleaching agents according to the present invention is compared with a conventional inorganic bleaching agent by washing stained fabrics with 1 litre water containing 4 gms of a detergent composition comprising linear alkyl benzene sulphonate 15%, sodium tripolyphosphate 37%, sodium silicate 6%, coconut monoethanolamide 3% sodium carboxymethylcellulose 1.5%, water 6% and balance sodium sulphate, the percentages being by weight, and sufficient active oxygen containing compounds to yield active oxygen in solution in the range 5—35 ppm. The washing is carried out at a temperature in the range of 30 to 60° C. and at a pH of 9. The active oxygen containing compounds consist of a) sodium perborate, b) diperoxyisophthalic acid (a and b included for comparison) and c) triperoxytrimesic acid. The fabrics comprise cotton or polyester cotton mixture, and the stains are conventional household stains. The stain removal is measured and broadly it is found that the order of stain removal is c)>b)>a) in the temperature range of 30 to 60° C. Typical results for red wine stains at pH 9 and 40° C. are tabulated below in which 100% stain removal represents restoring the reflectance of the stained cloth to the level before staining.

Av. Ox. content of solution (ppm)	Washing period (minutes)	% Stain Removal		
		(a) Sodium perborate tetrahydrate	(b) Diperoxyiso- phthalic acid	(c) Triperoxy- trimesic acid
5	10		58.5	62
10	10		62	73.5
15	10		72	81
20	10		74.5	84
25	10		79	89
30	10		80	90.5
35	10		80.5	91
100	10	52.5	—	—
5	30		71.5	77
10	30		79.5	87.5
15	30		85.5	94.5
20	30		90	99
25	30		92.5	101.5
30	30		94.5	102.5
35	30		95.5	103
100	30	66.5	—	—

WHAT WE CLAIM IS:—

1. A peroxyacid having the general formula I:—

5



wherein $p=3$, or 4

or salts thereof, the benzene nucleus being optionally substituted by an alkyl, chloro or nitro group.

10 2. A peroxyacid as claimed in claim 1 selected from 1,2,4-triperoxytrimellitic acid, 1,3,5-triperoxytrimesic acid, 1,2,3-triperoxyhemimellitic acid, 1,2,4,5-tetraperoxyphthalic acid and 1,2,3,4-tetraperoxyphthalic acid.

15

3. A peroxyacid as claimed in claim 1 or 2 which is in intimate contact with a desensitising amount of a desensitising diluent.

4. A peroxyacid as claimed in claim 2 wherein the desensitising diluent is granulated with the peroxyacid.

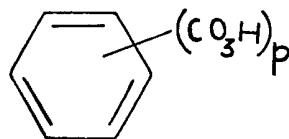
5. A peroxyacid as claimed in any preceding claim which is coated with from 3% to 35% by weight of a coating agent.

6. A bleaching or detergent composition comprising a surfactant, a builder salt, a bleaching agent and optionally containing a processing additive and detergent adjuncts selected from colouring materials, perfumes, bleach stabilisers, optical brightening agents, soil antiredeposition agents, enzymes, dedusting agents, tarnish inhibitors and abrasives, wherein the bleaching agent is a peroxyacid having the general formula I:—

20

25

30

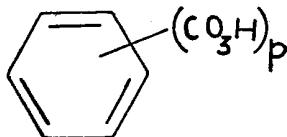


wherein p=3, or 4

salts thereof, the benzene nucleus optionally being substituted by an alkyl, chloro or nitro group.

5 7. A process for bleaching textile materials wood and pulp or cleaning hard surfaces with an aqueous solution of a peroxyacid having the general formula I:—

10



wherein p=3, or 4 or

salts thereof, the benzene nucleus optionally being substituted by an alkyl, chloro or nitro group.

15 8. A process according to claim 7 for treating a textile fabric, wherein the solution is aqueous and contains from 1 to 200 ppm available oxygen.

20 9. A process according to claim 8 wherein the aqueous solution is maintained at a temperature of from 20 to 60° C.

25 10. A process according to claim 8 or 9 wherein the aqueous solution is maintained at a pH of from pH 8.5 to pH 11.5.

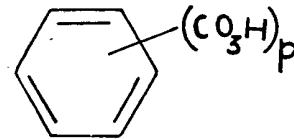
11. A process according to claim 7 and for treating a hard surface wherein the solution is aqueous and contains from 200 to 500 ppm available oxygen.

30 12. A process for bleaching textile materials wood and pulp or cleaning hard surfaces with

an aqueous solution of a peroxyacid as claimed in claims 1 to 5 substantially as described herein with respect to any single combination of process conditions given in the Example 1 (c).

13. A method of preparing a peroxyacid having the general formula I:—

35



wherein p=3 or 4

the benzene nucleus being optionally substituted by an alkyl, chloro or nitro group comprising the step of reacting an aromatic carboxylic acid having its acid groups located around the benzene nucleus at the position in which it is desired to obtain peroxy-carboxylic acid groups, with hydrogen peroxide in a non-aqueous polar solvent, provided that where the aromatic carboxylic acid contained two acid groups in ortho relationship an internal acyl peroxide is formed in the aforementioned step instead of two peroxy acid groups and in a subsequent step, the peroxyacid of the general formula I is generated in aqueous solution by perhydrolysis of the acyl peroxide.

14. Articles whenever cleaned or bleached using a peroxyacid claimed in any of claims 1 to 5, or using a bleaching or detergent composition claimed in claim 6 or a process for bleaching or cleaning claimed in any of claims 7 to 12.

40

45

50

55

60

A. N. CALDWELL,
Chartered Patent Agent,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.