PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C11D 3/39, D06L 3/02, C07C 409/24, 409/26, 409/30, D21C 9/16, A61L 2/00

A1

(11) International Publication Number: WO 94/18298

(43) International Publication Date: 18 August 1994 (18.08.94)

(21) International Application Number: PCT/GB94/00229

(22) International Filing Date: 7 February 1994 (07.02.94)

(30) Priority Data:
9302443.8 8 February 1993 (08.02.93) GB

(71) Applicant *(for all designated States except US)*: WARWICK INTERNATIONAL GROUP LIMITED [GB/GB]; Wortley Moor Road, Leeds LS12 4JE (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CROUD, Vincent, Brian [GB/GB]; 28 Woodland Drive, Greenfield, Holywell, Clwyd CH8 7HZ (GB). TOMPSETT, Stephen, James [GB/GB]; 5 Lower Bonc Terrace, High Street, Trelawnyd, Nr Rhyl, Clwyd (GB).

(74) Agent: JONES, Helen, Marjorie, Meredith; Gill Jennings & Every, Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).

(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GB, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: OXIDISING AGENTS

(57) Abstract

N-acyl compounds known as bleach activators especially tetraacetylalkylene diamines, are reacted with a peroxygen source in aqueous solution at an acidic pH to form an oxidising product which is a stronger oxidising agent than the peroxygen source used as the starting material. The product solution is used for instance as a bleach or disinfectant. The activator and peroxygen source may be provided as a concentrate product ready for dilution with components able to produce acidic pH in the aqueous solution. The product is, for instance in particulate solid form containing granules of activator and different granules of peroxygen source.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

Oxidising Agents

The present invention relates to the in situ production of peroxygen-based oxidising species from a peroxygen source and an activator followed by the use of the product as an oxidising agent, for instance as a bleach or a biocide.

It is very well known in the laundry detergent field to use a combination of peroxygen bleach precursor (or peroxygen source) and bleach activator in the same or separate compositions. The bleaching activators are acyl donors. The bleach precursor and activator, when added to the aqueous laundry liquor react together in a reaction involving attack by peroxide anion on the activator to form a peroxygen bleaching species usually the peroxy acid anion. The conditions of laundry liquors are invariably alkaline, usually having a pH of at least 9. The activator and peroxygen source do not react together during storage and are themselves stable under storage conditions.

It is known to coat or agglomerate bleach activators to increase their stability on storage in a laundry detergent composition and/or to affect their dissolution characteristics in the wash liquor. Fatty acids have been used and in WO-A-9213798 solid organic acids such as monomeric aliphatic hydroxy carboxylic acids including citric, lactic and glycolic acids, are incorporated into activator particles. In EP-A-0028432 bleach particles are stabilised for storage by incorporating acidic components. The particles are incorporated into conventional alkaline laundry detergents.

In Report no. R202, October 1992, of the Wool Research Organisation of New Zealand, the shrink proofing of wool by treatment with aqueous sodium perborate is described. The reaction is carried out at alkaline pH and in some instances tetraacetylethylenediamine is used as an activator. The effect of carrying out the treatment at neutral pH is investigated and it is concluded that that at

acidic pH the perhydroxy anion does not decompose to an active oxidising species. The concentration of sodium perborate in the aqueous solution is 0.1M whenever neutral or acidic pH was used. Acidification is by the introduction of acetic acid into the solution of sodium perborate.

In American Dyestuff Reporter, June 1992, 34-41, El-Sisi et al describe the activation of hydrogen peroxide used in the preparation of cotton fabrics in a desizing, bleaching and scouring step by urea. The effect of varying the pH between 4 and 10 is investigated. The concentration of peroxide is always 8g/l (0.24M) or less. The temperature of the reaction is 95°C. The mechanism of activator postulated in this disclosure is different from the mechanism which is thought to be responsible for the activation properties of compounds incorporated into laundry detergents as bleach activators.

Organic peroxy acids are well known as useful oxidising agents for a wide range of specific oxidation reactions that they perform in high-to-quantitative yield. A review of the various methods known for the preparation of peroxy acids is available in "Organic Peroxides", volume 1, D. Swern Ed, Wiley Interscience (1970) 313-335. Most of the reactions described use the corresponding carboxylic acid, the acid anhydride, the acid chloride or the aldehyde as the starting materials for instance for a perhydrolysis reaction using hydrogen peroxide. One of the reactions uses the alkaline perhydrolysis of imidazolides of carboxylic acids to form the peroxy carboxylic acids (Folli, U et al (1968) Bollettino, 26, 61-69).

It is known to produce peracetic acid, a strong oxidising agent, in situ by reaction of acetic acid and hydrogen peroxide, for instance to be used in epoxidation reactions. The advantage of using the peracid rather than hydrogen peroxide itself is that it is a stronger oxidising agent. Peracids are however unstable and can be dangerous to transport in bulk. The problem with the in situ

reaction of acetic acid and hydrogen peroxide is that water must be removed to drive the reaction or else a large excess of one of the reactants must be used, necessitating complex separation and recycling steps. Acetic anhydride has also been used in place of acetic acid as starting material for this in situ reaction. The conditions during the in situ reaction step and subsequent oxidation reaction will be acidic. Acetic acid and acetic anhydrides as starting materials for an in situ reaction require special precautions on handling and so are not suitable for use in a domestic environment. Acetic anhydride is water sensitive and so requires special storage conditions.

In US-A-3551087 and US-A-3374177 a process is described in which formaldehyde or a formic acid ester or formamide is reacted with hydrogen peroxide to form performic acid solution which is then used as a bleach. The reaction and the bleaching take place in an acidic environment. The bleaching process is part of the industrial dyeing process for wool and silk. Performic acid is, however, extremely unstable and even relatively dilute solutions can explode at ambient temperatures. It is furthermore corrosive and an irritant, as is formic acid, the by-product of the bleaching reaction. For these reasons formate activators are undesirable, especially for use in a domestic or other non-industrial context.

In EP-A-0545594 tooth whitening compositions are described which contain peroxy acetic acid as the bleaching agent. Compositions into which peroxy acetic acid itself is incorporated are acidic. It is suggested that the peroxy acetic acid can be generated in situ by the reaction in aqueous solution of tetraacetyl ethylene diamine and sodium perborate. In the specific examples of that embodiment of the invention the aqueous solution formed when the perborate and activator are dissolved is alkaline.

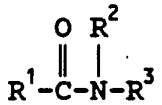
It would be desirable to find a system with the stability and advantages of the bleach precursor/activator combinations used in the laundry detergent industry, but

where the reaction between precursor and activator and/or the subsequent oxidation (including bleaching) step are carried out under acidic conditions and at relatively low concentrations.

In a new process according to the invention a peroxygen source is reacted with an activator compound which is an N-acyl compound in which the acyl moiety has at least 2 carbon atoms in a first step in aqueous solution under acidic conditions to form an oxidising product.

In the process the oxidising product is found to be a stronger oxidising agent than the peroxygen source.

In such a process the peroxygen source is reacted with an activator compound of the formula I

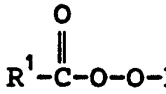


I

in which R^1 is an alkyl, aralkyl, alkaryl or aryl group, any of which groups has up to 24 carbon atoms and may be substituted or unsubstituted, and $-NR^2R^3$ is a leaving group in which R^2 and R^3 are independently selected from H, C_{1-24}-alkyl, -aralkyl, alkaryl or -aryl groups, and carbonyl-containing groups having at least 2 carbon atoms in which the carbonyl group is joined to the nitrogen atom in the formula I, in a first step in aqueous solution under acidic conditions to form an oxidising species which is a stronger oxidising agent than the peroxygen source itself.

Without being bound by theory, the present inventors believe that the mechanism of reaction is that the N-acyl activator is perhydrolysed, the N-containing part of the molecule acting as leaving group, to form the respective percarboxylic acid of the acyl group.

It is believed therefore that the product of the reaction of I with peroxygen source is a percarboxylic acid of the formula II



II

In one embodiment of the process, the product containing the stronger oxidising species is subsequently used as a bleaching agent in an aqueous environment at a pH of less than 7.

In another embodiment of the invention the product of the first step (hereinafter sometimes called the perhydrolysis step for convenience) is subsequently used as an oxidising agent in an oxidising step which is carried out without removal of any by-products from the first perhydrolysis step.

It is preferred that R^1 is an aliphatic group preferably a C_{1-18} alkyl group, or an aryl group.

In the present invention the term alkyl includes alkenyl and alkyl groups may be straight branched or cyclic.

In the compound of the formula I the groups R^2 and R^3 may be joined to form a cyclic group. R^1 may further or alternatively be joined to either R^2 or R^3 to form a cyclic group. These cyclic groups may include heteroatoms, for instance oxygen or optionally substituted nitrogen atoms, carboxyl groups as well as $-CH_2-$ groups or substituted derivatives thereof. They may be saturated or unsaturated.

Substituents on R^1, R^2 and R^3 can include hydroxyl, $=N-R^4$ in which R^4 is selected from any of the groups represented by R^2 and R^3 and is preferably lower alkyl, amine, acyl, acyloxy, alkoxy, aryl, aroyl, aryloxy, aroyloxy, halogen, amido, and imido groups and the like as well as other groups not adversely affecting the activity of the compound.

In the invention the compound of the formula I is preferably any N-acyl compound which has been described as a bleach activator for use in laundry detergents. The compound of the formula is preferably an amide derivative such as an acyl imidazolides as described by Folli et al (op cit) and N,N-diacyl amides, for instance, triacetyl ethanolamine or, most preferably tetraacetyl

ethylenediamine (TAED). Other examples of N-acyl derivatives are:

a) 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT);

b) N-alkyl-N-suphonyl carbonamides, for example the compounds N-methyl-N-mesyl acetamide, N-methyl-N-mesyl benzamide, N-methyl-N-mesyl-p-nitrobenzamide, and N-methyl-N-mesyl-p-methoxybenzamide;

c) N-acylated cyclic hydrazides, acylated triazoles or urazoles, for example monoacetyl maleic acid hydrazide;

d) O,N,N-trisubstituted hydroxylamines, such as O-benzoyl-N,N-succinyl hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl hydroxylamine and O,N,N-triacetyl hydroxylamine;

e) N,N'-diacyl sulphurylamides, for example N,N'-dimethyl-N,N'-dimethyl-N,N'-diacetyl sulphuryl amide and N,N'-diethyl-N,N'-dipropionyl sulphurylamide;

f) 1,3-diacyl-4,5-diacyloxy-imidazolines, for example 1,3-diacetyl-4,5-diacetoxy imidazoline, 1,3-diacetyl-4,5-dipropionyloxy imidazoline;

g) Acylated glycolurils, such as tetraacetyl glycoluril and tetraproprionyl glycoluril;

h) Diacylated 2,5-diketopiperazines, such as 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine and 1,4-dipropionyl-3,6-dimethyl-2,5-diketopiperazine;

i) Acylation products of propylene diurea and 2,2-dimethyl propylene diurea, especially the tetraacetyl or tetrapropionyl propylene diurea and their dimethyl derivatives;

j) Alpha-acyloxy-(N,N')polyacyl malonamides, such as alpha-acetoxy-(N,N')-diacetyl malonamide.

k) O,N,N-trisubstituted alkanolamines, such as O,N,N-triacetyl ethanolamine.

l) N-acyl lactams, such as N-benzoyl-caprolactam, N-acetyl caprolactam, the analogous compounds formed from C_{4-10} lactams.

m) N-acyl and N-alkyl derivatives of substituted or unsubstituted phthalimide, succinimide and of imides of

other dibasic carboxylic acids, having 5 or more carbon atoms in the imide ring.

In the process of the invention the precursor peroxygen source may be hydrogen peroxide itself, but is alternatively an inorganic persalt, for instance a percarbonate or a perborate, for instance sodium perborate, or an organic peroxide such as benzoyl peroxide or urea peroxide.

The pH in the perhydrolysis step is preferably less than 6.5 throughout the entire reaction. Since the pH tends to drop during the reaction due to the formation of the percarboxylic acid, this means that the pH should be acidic and preferably less than 6.5 at the beginning of the reaction. Preferably the pH is less than about 6.0, at the start of the reaction. The pH is usually more than 2.0, at the start of the reaction and preferably throughout the reaction, preferably more than 5.0.

In the perhydrolysis reaction the amount of water present is preferably at least as much as (in terms of moles) as the peroxgyen source. Where the peroxygen source is hydrogen peroxide itself, the concentration of hydrogen peroxide is preferably less than 70% weight/volume (that is weight of hydrogen peroxide based on volume of water plus hydrogen peroxide plus other components in the mixture concerned). Preferably the concentration is less than 60% weight by volume and more preferably less than 30% w/v. Where the product of the reaction is to be used in a domestic environment or other environment where it is difficult to take special precautions in handling the products, it is preferred for the concentration to be less than 15 or even 10% w/v for instance 5% w/v or less. The concentration is usually at least 0.2%, preferably at least 1% w/v, more preferably at least 2% w/v. Where the peroxygen source is other than hydrogen peroxide then the concentration is preferably such as to give the equivalent available oxygen as the quoted concentrations of hydrogen peroxide. Expressed in molar terms, for instance, the

concentration of hydrogen peroxide or perborate or percarbonate is suitably in the range 0.01M to 10M, preferably in the range 0.05 or 0.1M to 5M, more preferably in the range 0.2M to 2M often less than 1M, in the perhydrolysis reaction mixture.

In the perhydrolysis step of the reaction the temperature is preferably in the range 0 to 95°C, more preferably in the range 10 to 80°C. The invention is most useful when the temperature is less than 60°C, or even less than 50°C, for instance less than 40°C or even around room temperature. The temperature is often above 20°C. The temperature in any subsequent oxidising step is preferably in the same ranges as the temperature during the perhydrolysis step and is preferably substantially the same temperature especially where the product solution is immediately used for instance as a bleach or disinfectant. A particular advantage of using activators for the peroxygen source is that the oxidising product tends to be formed at a relatively low temperature, for instance less than hand hot which is advantageous from a safety point of view.

The activator compound is generally used in an amount such that it is capable of providing in the range 0.1 to 5.0 equivalents of acyl groups based on the moles of peroxygen source, preferably in the range 0.2 to 1.0. The amount is often less than stoichiometric, for instance up to 0.9 or 0.8 of the stoichiometric amount. For instance tetraacetyl ethylenediamine reacts as an activator to donate one acyl group from each nitrogen atom and so to provide 0.2 equivalents acyl groups per mole of peroxide, 0.1 mole of TAED is needed for total reaction. Often less than this is used, although the optimum amount depends upon the degree of increase in oxidising performance compared to the costs of the peroxygen source and activator.

The present invention provides also use of a composite product comprising all the starting materials for the perhydrolysis reaction. Preferably the product can simply

be added to water to provide the entire reaction mixture. The product therefore comprises a peroxygen source, an N-acyl activator compound preferably of the formula I, as well as components for rendering the pH of an aqueous solution to which the components of the product are added acidic if necessary, though in some circumstances the peroxygen source itself may be sufficiently acidic that no extra acidifying component is needed.

An acidifying component may comprise an acid and/or buffering material. The component may comprise a polybasic organic acid, such as a polybasic carboxylic acid such as citric, succinic, or adipic acid or sulphamic acid. Alternatively the component may react with a by-product of the perhydrolysis reaction to make an acid. Where perborate is used, borate is a by-product and so any component known to react with borate to drop the pH, eg cis-1,2-diols, eg glycols and polyols, boric acid or sodium dihydrogen phosphate, can be used. Such acidifying components are also suitable for use with other inorganic persalts.

Although the composite product may contain the individual components in two or more separate compositions, for instance one of which contains the peroxygen source (for instance an aqueous solution of hydrogen peroxide as a concentrate for dilution or ready for use without further dilution) and another of which contains the activator, for instance of the formula I, it is preferred for a mixture of at least two of the components to be provided in a single composition, in which the components do not react, and which is preferably substantially waterfree. It is preferred to provide at least the activator and acidifying component, if any, as a mixture in a single composition in a form in which they are stable. Such a product which does not contain peroxygen source, may for instance, be added to an aqueous solution of peroxygen source, such as hydrogen peroxide, which is readily commercially available, in the form of 60%, 20% 10% or, preferably 5% w/v, or less,

solution. It is most preferred for the activator, peroxygen source and any acidifying component to be present in a single composition.

The products may be in liquid form, for instance in a non-aqueous liquid medium, in which the components may be dissolved or dispersed. For instance particles of activator with protective coatings, for instance produced by microencapsulation techniques or spray coating of solid activator, may be suspended in an aqueous, or non aqueous, solution of peroxygen source. As an alternative to a solution of peroxygen source that component may also be suspended in the liquid medium, either in a separate liquid phase or in particulate dispersed phase, particles of solid peroxygen source optionally being coated with a protective coating. Coated particles of either peroxygen source or activator may be disrupted simply by being diluted into water or physically disrupted by applying abrasion.

Preferably the product is in solid form, for instance as a mixture of particles of the individual components or, more preferably, comprising particles each of which comprise all of the components. Such particles may be provided by techniques similar to those used in the laundry detergent industry, for instance including particles produced by spray drying liquid slurries, by granulation techniques using binders for instance synthetic or natural polymers (or derivatives) or by melt blending followed by extrusion or other techniques.

The composite product may include other additives, for instance stabilisers which stabilise the product before use, as well as stabilisers for the stronger oxidising species formed in the reaction, especially heavy metal sequestrants. The new product may also include surfactants to act as wetting agents and inorganic salts, for instance which affect the physical properties of the solid form or act as diluent or to increase the rate of disintegration of dissolution of the product. Other ingredients may be included depending on the form of the product and the final

application of the reaction product, for instance perfumes, abrasives.

Preferably the product contains the active ingredients in appropriate relative quantities so that when the composition is diluted (or the compositions are mixed) with water the first step of the reaction proceeds at the optimal rate and at the desired pH. The activator and peroxygen source are for instance present in relative amounts such that 5% to 150% of the stoichiometric amount of activator (for complete reaction with the peroxygen source) is provided. Preferably the amount of activator is 10 to 100%, more preferably 20 to 80% of the stoichiometric amount.

The reaction product of the perhydrolysis reaction is preferably used immediately, without removal of any by-products or addition of other materials, in a second step in which it is used as an oxidising agent, bleaching or disinfecting agent. Sometimes it may be desirable to add additional ingredients for the second step such as pH-adjusters, and surfactants/wetting agents which may cationic, anionic, amphoteric or non-ionic. Other additives which may improve the second step of the process are for instance disinfectants, biocides, slimicides, enzymes, inhibitors or radical scavengers, abrasives etc. Cobiocides are particularly valuable where the primary objective of the second step is disinfection/ sterilisation.

The second step of the process of the present invention may be used as a bleaching/disinfection process, by which we mean any process in which unwanted colour is reduced or removed, non-coloured stains are reduced or removed and/or a substrate is disinfected. For instance the second step may include processes in which hard surfaces in domestic, industrial or institutional applications are cleansed, fabrics (for instance during fabric manufacture and dyeing) or the solution is used in water, effluent or sewage treatment as a biocide, in pulp

and paper bleaching, paper deinking, wood bleaching, in fibre and fabric manufacture, a biocide, fungicide, bacteriocide, sporicide and/or viricide, as a contact lens disinfectant or general disinfectant for use inter alia in general environmental clean up. Furthermore the second step may be used in food production for instance to bleach flour, beverages, or edible oils in the food and brewing industries, for instance to clean pipes used for beverages, or, in cosmetic uses such as hair bleaching or tooth or denture whitening and disinfecting. The product of the first step may alternatively be used as an oxidising agent in organic synthesis eg for use in epoxidation reactions of alkenes or as a catalyst. It can be used as a curing agent for certain adhesives.

Since the reaction can be carried out at a relatively low concentration it can be carried out without special precautions, for instance in a domestic or institutional environment.

Compositions which are suitable to be diluted direct into water to allow the first and second steps of the reaction to proceed without further additions, may be categorised in four convenient categories.

The first category comprises liquid formulations which include a surfactant. These compositions will be suitable for use as hard surface cleaners and other uses where surface active disinfection and/or bleaching is required, for instance floor cleaning compositions, domestic and institutional hard surface cleaners, toilet disinfectants, general toiletries disinfectant, sanitising bottles, including glass and plastic bottles, and pipe cleaning compositions. For most of these uses it will be desirable for the composition to be relatively low foaming, although for some, for instance toilet disinfecting and general toiletries disinfectant, it may be desirable for the composition to have a relatively high foam. The use of suitable surfactants which will foam is well known in the art. For compositions which are desired to be low foam, it

may desirable to incorporate anti-foaming agents, for instance soap or silicone anti-foams. Liquid formulations including surfactants may be useful in other applications such as for use to bleach fibres or fabrics, such as nappies or in fabric production, cellulose fibres, especially in paper de-inking operations, and in general environmental clean-up operations.

A second category of composition comprises liquid formulations but which contain no surfactants. These may be useful where no surface activity is necessary, for instance in effluent and water treatment, in toilet disinfectants, for use as a swimming pool treatment, for colour removal from chemicals, from pulp during paper making or recycling, in general industrial sterilisation and in some domestic sterilisation situations, for instance as a general toiletry disinfectant, in denture cleaning compositions, in sanitising glass and plastic bottles or other containers, as well as in certain environmental clean-up operations. Furthermore, where the composition is to be used as a general industrial oxidation reaction, it may be undesirable to include a surfactant.

The liquid formulations mentioned above may be pourable liquids, which are aqueous or non-aqueous, or may be in gel or paste form. Furthermore the compositions may be two-phase, for instance a cream form. Alternatively the compositions could be in the form of a mousse (where the composition contains surfactant) by the injection of a gas, especially for domestic hard surface cleaning operations.

A further category of composition is in solid form and includes a surfactant. The general uses of these compositions are similar to those for which the liquid formulations including a surfactant are useful, as mentioned above.

A further category of formulation comprises a solid composition but without surfactant. These compositions are useful in the same categories of uses as the liquid formulations without surfactant. The compositions may, in

solid form, be more storage stable, since it is in general easier to keep the bleach activator and peroxygen donor compound in separate particles and prevent them coming into contact with one another during storage. It is furthermore easier to isolate other components of the composition from one another and from the bleach components, especially where storage sensitive compounds such as enzymes, other biocides or perfumes are present.

Solid compositions may be in the form of particulate mixtures or may be tabletted. Tabletted formulations, or even granular formulations, may include agents to increase the dissolution rate of the compositions upon addition to water. For instance suitable components incorporating into tablets aid disintegration of the tablet. Such ingredients may create effervescence, for instance; a suitable component is sodium bicarbonate, or other alkali metal bicarbonate.

The compositions may also contain ingredients to assist in their application or stability or which improve their appearance, for instance thickeners, dispersants, opacifiers, hydrotropes, dyes, perfumes etc.

The following examples illustrate the invention. In the example the concentration of the peroxygen source is reported in terms of the starting concentration of aqueous hydrogen peroxide, to which other reactants are added. The molar concentration of the mixtures can be calculated.

Example 1

Reaction of TAED and hydrogen peroxide

1.1 This area of investigation was to find a simple method of determining the presence of a stronger oxidising species than hydrogen peroxide. To this end a number of indicators containing oxidisable groups were tried, to identify which changed colour on addition of peracetic acid and the oxidising product of an embodiment of the invention, but not hydrogen peroxide. The results showed that alizarin complexone (AC) was decolourised by peracetic acid, but not

by hydrogen peroxide. This material was therefore selected as the indicator of choice.

1.2 Once an indicator had been identified it was possible to carry out the experiments to see whether acid catalysed perhydrolysis was a possible mechanism. TAED (22.8g 0.1mol) was added to 60% hydrogen peroxide (60mls 1mol). The mixture was stirred for 10 minutes. A 2ml aliquot was removed and added to alizarin complexone solution (0.5ml). Over a period of a few minutes the colour in the solution was seen to disappear as the indicator was bleached.

1.3 The successful result of this experiment led to comparative bleaching experiments being carried out on stained swatches of cloth. The stains used were Red Wine, Tea and BC1 (tea and clay). Comparisons were made between the bleaching performance of 60% H_2O_2, 10% peracetic acid PAAH and TAED/H_2O_2. The performance was assessed by measuring the initial brightness before washing and final brightness using a Hunterlab D25M colorimeter after the swatches had been rinsed and dried by application of an electric iron set at the wool setting. The results are given in Table 1.

1.4 Another set of experiments determined at which initial pH was the greatest bleaching observed. These experiments were carried out in 60ml 60% H_2O_2 with 22.8g TAED added. The pH of the peroxide was adjusted before the addition of TAED with sodium hydroxide. The highest pH attainable was 6.95 as above this the decomposition of the peroxide was too rapid. The stain used in these tests were tea stains produced in house. These were selected as they showed the greatest residual colour in the previous tests. The pH of the solutions were measured initially after 1 hour's bleaching after 3h and finally after 24h. All bleaching experiments were carried out at room temperature. A blank was run using distilled water at pH 6. The results are shown in Tables 2 and 3.

1.5 Experiments were also carried out to identify whether Fe(III) ions had an effect on the bleaching properties.

Three systems were set up, one containing Dequest 2066 (an alkylene polyamine polylmethylene phosphonic acid) as a sequestering agent, one with 0.5mls 20mM Fe(III) solution added and one with hydrogen peroxide only. All of these were carried out at pH 6. The results are shown in Table 3.

1.6 Results & Discussion

All experiments carried out at room temperature in open beakers. Dwell time in the bath of 1 hour.

Table 1

Example	Stain	Red Wine		Tea	
	Bleaching solution	Initial Brightness	Final Brightness	Initial Brightness	Final Brightness
1.1	TAED/H_2O_2 60%	46.5	74.8	25.0	63.9
1.1 comp	H_2O_2 Comp	46.5	69.7	25.8	46.6
1.2 comp	PAAH	46.5	76.7	25.7	61.0
1.3 comp	HCl	46.5	63.9	-	-

Table 2

BC1 Stains (Tea and Clay)

Example		pH after time				Initial Brightness	Final Brightness
	Bleaching solution	Initial	0.5hr	1.5hr	46hr		
1.2	TAED/60% H_2O_2	1.21	1.28	1.71	2.64	38.5	53.8
1.4 Comp	60% H_2O_2	1.21	-	-	-	38.5	48.9

Table 3

Tea Stains

Example	Bleaching solution	pH after time				Initial Brightness	Final Brightness
		Initial	1hr	3hr	24hr		
1.3	TAED/60% H_2O_2	2.5	2.48	3.12	2.68	25.8	72.8
1.4	TAED/60% H_2O_2	3.15	2.76	3.40	2.71	24.9	76.1
1.5	TAED/60% H_2O_2	4.54	3.03	3.30	2.68	26.8	77.8
1.6	TAED/60% H_2O_2	5.13	3.18	3.20	2.70	24.9	79.1
1.7	TAED/60% H_2O_2	6.0	3.33	3.26	2.80	24.4	82.9
1.8	TAED/60% H_2O_2	6.95	3.58	3.70	3.35	24.8	84.8
1.9	TAED/60% H_2O_2/Seq	6.05	2.83	2.65	-	26.8	82.7
1.5 Comp	60% H_2O_2/Fe(III)	6.22	6.07	6.08	-	24.3	75.6
1.6 Comp	60% H_2O_2	6.19	6.11	6.13	-	25.4	75.8
1.7 Comp	Deionised Water	5.96	-	-	-	23.4	33.7

Notes: With 60% hydrogen peroxide and TAED at the higher end of the acidic pH range bleaching was visible on contact, with the other solutions the bleaching was much less rapid. On reaction there was effervescence visible as the TAED dissolved, this process was much more rapid at higher pH. There was a distinct odour of peracetic acid from all reactions containing TAED. Remarkably the bleaching activity towards AC was still observed after 24 hours at room temperature.

1.7 These results show that TAED activates peroxide solutions at a range of pH's. The quickest bleaching performance is seen at higher pH probably due to more rapid dissolution of TAED and formation of stronger oxidising species under these conditions. The formation of an acidic species when TAED is dissolved in hydrogen peroxide is indicated by the pH change observed, the solutions only become markedly more acidic if TAED is present. Those experiments carried out without TAED show very little change in pH on the same time scale. The noticeable odour of peracetic acid, which is rather distinctive as well as pungent, is also evidence for the presence of this species in solution. It is assumed from this evidence that peracetic acid is likely to be the bleaching/oxidising species responsible for the bleaching effect, although it may be a by-product, an intermediate or the product of further reaction of another oxidising species.

1.8 The experiments with and without Fe(III), at pH 6, showed very similar bleaching (the %ge stain loss was identical). This seems to show that iron catalysed radical reactions are not important under these conditions. This conclusion is borne out by the results with sequestrant present which gave very similar results to the experiment without sequestrant at pH 6.

Example 2

TAED and DADHT as activators for peroxygen bleaches at acidic pH, for stains in solution and on fabrics

2.1 Experimental

2.1.1 Swatches

The activator/peroxygen source combination procedure used was 60% hydrogen peroxide in a 10:1 ratio with the activator. Small swatches of cloth (20-25cm^2) were used and the stain was chlorophyll. The bleaching experiments were run using 10mls hydrogen peroxide (60%) which was adjusted to the required pH using sodium hydroxide solution. A weighed quantity of the activator (16.7 mmol) was then added and the mixture stirred for 2 minutes to dissolve the activator. The swatch of cloth was then added and left for 30 minutes with occasional stirring. After 30 minutes, the swatches were removed from the activator solutions, rinsed with deionised water to remove any remaining traces of bleach, dried by the technique used in example 1 and the brightness measured using a Hunterlab D25M colorimeter. The pH of the solution was measured after the cloths had been removed. The results are shown in Table 4.

2.1.2 The dependence of pH on time

Experiments to monitor the relationship between pH and time were carried out using TAED and DADHT as activators. The pH of 60% hydrogen peroxide was adjusted to about pH 6. To 20mls of this solution was added 33m mols of activator. The pH was measured with time.

2.1.3 Timed bleaching

Timed bleaching experiments were carried out using the same technique and quantities as in 2.1.1 above with different dwell times of the swatch in the bleach solution. Six separate solutions were prepared and a swatch added to each at the same time. The swatches were removed and rinsed in deionised water after set time periods. The times used were 5mins, 10mins, 20mins, 30mins, 1hr and 2hrs. The final brightness after drying by the usual

technique was determined using the Hunterlab. The results are shown in Table 5.

2.1.4 Time/pH bleaching profile

The solutions and swatches used were prepared as in the above experiments. Four solutions were prepared and a swatch added to each after a set period of time. The cloth was left in the bleach solution for 5mins and then removed and rinsed thoroughly with deionised water. The times at which the swatches were added were after 1min, 15mins, 30mins and 1hr. A different solution was used for each swatch. The activators used were TAED and DADHT. The final brightness after drying of the cloth was measured using the Hunterlab. The results are shown in Table 7.

2.1.5 Activation of sodium perborate solutions in the presence of acidifying components.

Two lots of sodium perborate tetrahydrate (17.5g) mixed with citric acid (8g) (to reduce the pH on reaction with borate) were prepared. To one lot TAED (2.6g) was added. Each of the mixtures was added to 50mls deionised water and stirred vigorously. The pH of the solutions was measured after dissolution had been achieved. The results are given in 2.2.6 below.

2.2 Results and Discussion

2.2.1 The chlorophyll stain was seen to be resilient to bleaching under these harsh conditions which makes it a very good stain to use. The less stain that is removed the better the comparisons which can be drawn between bleaches.

2.2.2 DADHT reacted faster than TAED, see table 7. The blank experiments with peracetic acid, water and hydrogen peroxide (at both pH 6 and pH 1) show that activation is occurring, when the activator is present, and that this is not an effect of the lower pH in the activated solutions (Table 4). The drop in pH is good evidence that an acidic species is being produced which is not present in the unactivated peroxide solution.

2.2.3 The decrease in pH on addition of activator was seen to be rapid (Table 6). As would be expected the rate

varied with different activators due to differences in both the acid being produced and the rate of perhydrolysis.

2.2.4 The bleaching of swatches with different bleaching times showed the expected increase of bleaching with time (Table 5).

2.2.5 The effect of time and pH on the bleaching efficacy of activated solutions was also studied. In this case the dwell time in the bleaching solution was the same (5 mins) but the swatches were added after different times. In four separate solutions cloth was added after 1min, 15mins, 30mins and 1hr. Each of these swatches was a quarter of the same larger swatch, to ensure a constant substrate concentration. After 5 minutes in the bleaching solution the cloth was removed and rinsed with deionised water. Comparing of the different swatches, for the same activator, gave a measure of the stability, rate of peracid release and pH dependence of the bleaching. The relationship between these variable is complex but qualitative comparisons can be made. The results show that TAED gives consistent bleaching over the first hour. DADHT on the other hand gives better initial bleaching but after an hour the efficacy was similar (Table 7). This seems to show that DADHT is perhydrolysed more rapidly initially but after time gives a similar concentration of peracid. This is borne out by the pH measurements. The pH of the solution containing DADHT decreased more rapidly than that of the TAED containing solution. After 20hrs the figures were much closer (Table 6).

2.2.6 The activation of sodium perborate solutions was also seen to occur under acidic conditions. The use of citric acid and sodium dihydrogen phosphate enable acidic solutions of perborate to be prepared which also give rise to some degree of buffering. The pH of the solutions was seen to be acidic (pH 5.1) and much more stable than seen with more concentrated peroxide solutions. The pH of the activated and unactivated solutions was very similar.

Table 4. Activating acidic peroxide with different activators.

Example	Activator	Initial pH	Final pH	Initial Brightness	Final Brightness
2.1	TAED (30min)	6.00	2.47	14.26	38.4
2.2	DADHT	6.00	2.33	14.26	61.3
2.1 Comp	Blank (H_2O_2)	6.00	5.96	14.26	30.9
2.2 Comp	Blank (H_2O)	7.50	5.68	14.26	19.7
2.3 Comp	Blank (PAAH)	-	-	14.26	59.2
2.7	TAED (10min)	6.00	-	14.26	21.8

Table 5. The effect of different bleaching times on brightness and solution pH.

Time/ mins	Final brightness		pH after 2 hrs	
	TAED	DADHT	TAED	DADHT
5	27.8	48.8	3.21	3.15
10	33.5	57.4	3.09	3.15
20	46.2	60.6	3.20	3.17
30	52.2	68.2	3.15	3.15
60	57.1	79.8	3.18	3.21
120	74.1	84.5	3.21	3.14

Table 6. The effect of activators on solution pH with time.

Time/ mins	pH	
	TAED	DADHT
0	6.18	6.05
1	5.29	4.83
2	5.03	4.50
3	4.85	4.23
5	4.62	3.96
7	4.47	-
9	4.35	-
10	4.31	-
20	4.00	-
23	-	3.26
30	3.86	-
40	-	3.11
65	3.64	-
1200	3.27	2.54

Table 7. Bleaching efficiency against time.

Time/ mins	Initial Brightness	Final Brightness	
		TAED	DADHT
1	14.26	32.0	34.1
15	14.26	31.9	32.7
30	14.26	28.7	26.9
60	14.26	25.8	20.9

DADHT - 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine

Example 3

Biocidal activity of activator/hydrogen peroxide mixtures

3.1 The assessments were performed in a test tube situation following the principles of BS 6471:1984.

3.2 100ml volumes of Nutrient Broth were inoculated with Escherichia coli, Staphylococcus aureus and Streptococcus faecalis.

3.3 A 150mg/l solution of peracetic acid (PAA) was used for comparison. This was prepared in sterile distilled water.

3.4 In order to achieve concentrations comparable with the comparative 150mg/l PAA solution, test solutions of the formulations were prepared using TAED in the amount noted in the table below 0.0225g of TAED in 100ml 1% hydrogen peroxide solution. In example 3.6 the test solution was left to age for 24 hours before use. The other test solutions were used immediately.

3.5 1ml of the test bacterial culture was added to 9ml of the appropriate formulation, mixed and left for 5 or 10 minutes at room temperature or at 40°C (as indicated in the table).

3.6 1ml of this liquor was transferred to 9ml of inactivator comprising 50g/l sodium thiosulphate and 0.25g/l catalase in distilled water. The inactivator was filter sterilised using 0.45μm membrane filters.

3.7 From these inactivated liquors, 10-fold serial dilutions were performed using Maximum Recovery Diluent (MRD). Pour plates were prepared using 1ml volumes of each dilution mixed with molten Plate Count Agar (PCA).

3.8 For controls the procedure was repeated using 1% hydrogen peroxide as the control for the two formulations and sterile distilled water as the control for PAA.

3.9 All plates were incubated for 48 hours at 37°C after which time the number of colonies visible on each plate was counted. The reduction in the number of CFU compared to the control solution is calculated. The results quote the log (base 10) of the control count/test count. Where the figure is "more than" the actual figure quote this indicates the CFU count on the test plate was below the minimum which can be quantified by this technique.

Results

Table 8 - Biocidal efficiency

Example	TAED amount (g/100ml H_2O_2)	Time min	Temperature	Log Reduction rates		
				E.coli	Staph.aureus	Strep.faecalis
3.1	0.0225	5	room	1.54	0	0.70
3.2	0.30	5	room	0.34	0	0
3.3	0.03	5	40°C	4.21	2.02	>4.96
3.4	0.03	10	room	0	1.13	2.23
3.5	0.15	10	room	>5.19	0.54	>5.81
3.6	0.03	10	room	>3.42	0.89	>4.60
3.7	peracetic acid	5	room	>6.83	1.68	>6.46

3.10 TAED/H_2O_2 generally did not appear to be particularly effective when compared with PAA at room temperature for short contact times although some reduction was seen against E.coli and Staph. aureus.

3.11 Increasing the temperature to 40°C improved the performance of TAED.

3.12 Increasing the contact time from 5 minutes to 10 minutres and so improved the results.

3.13 By aging the solution for 24 hours before use the same improvement was seen as by increasing the temperature. This improvement may be a result of the slow release properties of the system.

Example 4

Production of Acidic Percarbonate solutions

4.1 It has been found that citric acid and sodium dihydrogen phosphate are able to produce acidic solutions of hydrogen peroxide when mixed with sodium perborate and water. This experiment was designed to test whether the same was true for sodium percarbonate.

4.2 The following formulations were added to 1ℓ cold water. In each case 1.85 g TAED, as activator was included. The amount of percarbonate was varied, with the amount of citric acid added being such as to give approximately the same pH in each test. The presence of hydrogen peroxide was determined by iodometric titration as described in Example 5 below.

TABLE 9

Sodium Percarbonate g	2.05	4.13	8.20
Citric Acid g	1.54	3.08	6.04
Time mins	Iodometric Titrations		
5	0.5	0.7	1.2
15	1.2	2.35	4.3
30	2.9	6.80	9.9
45	5.4	12.05	14.9
60	17.5	17.80	21.7
ph at 10 mins	6.39	6.38	6.35

Example 5

Acids and anhydrides as activaters

5.1 Using acetic acid (comparative) and TAED (invention) as the acetyl donor.

The following experiments were carried out using 50ml 10% w/v hydrogen peroxide at room temperature with activator and compared against controls. Chlorophyll stained swatches were used as the substrate. Reflectance was measured using an ICS Texicon Spectra Flash 500 (a colorimeter using the CIELAB system) using software version 4.70.

The initial pH's of these solutions were recorded.

The swatches were left in solution for 75 minutes. The brightness was compared to an unbleached chlorophyll stained swatch after rinsing with deionised water and drying as in the previous examples.

Results

Table 10

Example	Reading	Solution	Activator	Initial, pH
5.1.1	1.6 lighter	50 ml H_2O_2	TAED 3.17g	3.35
5.1.2 Comp	0.35 lighter	50 ml H_2O_2	Glacial Acetic 1.67g	2.32
5.1.3 Comp	0.75 lighter	50 ml H_2O_2	-	3.33
5.1.4 Comp	0.2 darker	50 ml H_2O	Glacial Acetic 1.67g	2.62

It can be seen that acetic acid is ineffective as an activator under these conditions. This experiment also shows that the bleaching effect of TAED does not arise from hydrolysis followed by perhydrolysis of the resulting acetic acid.

5.2 The use of acetic anhydride (comparative) and TAED (inventive)

Acetic anhydride is a widely used source of peracids under laboratory conditions. This material is however water sensitive, corrosive and therefore not easy to handle. The following experiments were designed to see how effective acetic anhydride was as a peracid generator under dilute aqueous conditions.

The procedure used was similar to that in the above experiments (5.1) with acetic acid. Hydrogen peroxide was used at 10%. A range of stained swatches were used, these were chlorophyll, curry and blackberry. Samples were also assayed for peracetic acid using an iodometric titration.

5.2.1 Bleaching stained swatches

In the following experiments the peroxide/activator combinations shown in Table 10 were used to prepare the bleaching solutions.

All experiments were carried out at ambient temperature. Formulation 5.2.4 Comparative was only used

in the first two experiments. The reflectance was measured as in 5.1. In the table the reflectance differences are noted. A positive value means the bleached swatch is lighter than the control stained swatch and a negative sign means it is darker.

Experiment A

Chlorophyll stained swatches were added to these solutions and left to bleach for 75 mins. After this time the swatches were removed and washed in water to remove any remaining active species.

Experiment B

Chlorophyll stained swatches were added to the solutions used above and left to bleach overnight for 17 hours. The swatches were rinsed. The pH of the bleaching solution was measured after the cloths had been removed.

Experiment C

Fresh solutions using the first three compositions were prepared and allowed to stand overnight before chlorophyll stained swatches were added. The cloths were left to bleach for 75 mins and then removed and rinsed.

Experiment D

This was the same as experiment A but using curry stained swatches. There was no water/acetic anhydride solution (5.2.4 comp) tested.

Experiment E

This was the same as experiment A using blackberry stained swatches. There was no water/acetic anhydride solution (5.2.4 comp) tested.

5.2.2 Iodometric titration

The solutions 5.2.1 and 5.2.2 (comp) used in experiment E were tested after given time intervals for peracetic concentration using an iodometric titration on ice so that hydrogen peroxide gives minimal values alone) the titration being carried out as soon as possible after the titration mixture is made up.

5.2.3 Results

Table 11

Experiment	Solution	Activator	pH	Reflective Difference				
				A	B	C	D	E
5.2.1	50ml H_2O_2	3.17g TAED	3.47	1.3	4.4	0.38	1.3	8.6
5.2.2 Comp	50ml H_2O_2	2.4g acetic anhydride	2.10	3.2	8.6	1.6	1.3	10.2
5.2.3 Comp	50ml H_2O_2	-	3.69	0.6	1.0	0.67	1.2	8.2
5.2.4 Comp	50ml H_2O	2.4g acetic anhydride	-	0.48	-0.4	-	-	-

In general acetic anhydride/H_2O_2 reacted more quickly than either TAED/H_2O_2 or H_2O_2 itself. TAED/H_2O_2 gave better bleaching against chlorophyll stains than H_2O_2 alone.

5.3 Determination of the peracetic acid produced by acetic anhydride (comparative) and TAED.

The relative concentration of oxidising agent was determined at time intervals using an iodometric titration on ice. The solutions studied were those used in experiments 5.2.1 and 5.2.2 Comp Experiment E as 5.3.1 and 5.3.2, respectively. The iodometric titration carried out was that used for calibrating peracetic acid. The solution to be assayed is added to a flask containing potassium iodide, acetic acid and ice. The iodine liberated is titrated with sodium thiosulphate.

Table 12

Time/hr	Relative amount of strong Oxidising agent	
	5.3.1 (TAED)	5.3.2 (acetic anhydride)
1.5	0.19	1.16
3.75	0.23	1.37
20.75	0.61	1.56
26	0.70	1.43
92	0.72	0.91
117	0.91	0.76
168	1.22	0.57

It can be seen from the above results that the TAED activated solution gives a lower initial concentration of strong oxidising agent. However over time, in this case 7 days, the TAED solution increases in strong oxidising agent concentration while the acetic anhydride solution loses peracid. After several days the levels of strong oxidising agent acid are higher in the TAED containing solution. There is still a large volume of TAED left undissolved after about 140 hrs. This makes this a very good slow release procedure.

Example 6

Perborate/TAED in a non-surfactant containing composition

A mixture of the following powders was made and added to 1ℓ of water:

1.8 g TAED

2.58 g sodium perborate monohydrate

without or with 1.58 g sodium bicarbonate

varying amounts of citric acid or sodium dihydrogen orthophosphate as acidifiers. The pH of the solution at the varying amounts of acid component were measured after 10 mins. The results are shown in the following table.

TABLE 13

Acidifier	Bicarbonate	pH														
		1	2	3	4	5	6	7	8	9	10	12	14	16	18	20
Citric Acid	Yes	8.6	7.2	6.0	5.4	4.9	4.8	4.4	4.3	4.0	3.9	-	-	-	-	-
Citric Acid	No	8.5	6.5	5.1	4.6	4.3	4.1	3.9	3.6	3.5	3.5	-	-	-	-	-
NaH_2PO_4	-	-	8.7	-	7.9	-	7.1	-	7.0	-	6.6	6.6	6.4	6.3	6.3	6.2

The bleaching performance of some of the solutions was determined on un-glazed, tea-stained tiles. The bleaching solution is applied to one half of the tile and the difference in whiteness, as determined using a Hunter-Lab apparatus between the two halves is determined. The value is given as ΔW. The Hunter-Lab apparatus is set to CIE tristimulus XYZ scale. The W reading is the Z% brightness.

The solution as above with bicarbonate, which had a pH of 6.3 gave a ΔW value of 5.5.

Example 7

Surfactant - 3 Compositions Including Perborate and Various Activators

Mixtures containing 2.58 g sodium perborate monohydrate, 3 g citric acid, 1.6 g sodium bicarbonate and activator comprising 1.8 g TAED or an equivalent weight of N-benzyl caprolactam (NBC) or triacetyl ethanolamine (TAE) or granules containing TAED, were dissolved into 1ℓ water. The peracid release rate was monitored using an iodometric titration on ice, as above. The results are given in the following table.

TABLE 14

	Oxidising agent amount for the following activators				
Time	TAED	TAE	NBC	Granule 1	Granule 2
5	0.7	0.4	0.45	0.4	0.75
15	1.9	0.3	0.85	1.6	1.0
30	4.1	0.25	0.7	4.3	2.5
45	8.1	0.35	1.2	8.1	4.5
60	11.4	0.45	1.8	12.2	6.7
1 DAY	20	0.5	8.0	11.6*	18.8

* RESULT AFTER 3 DAYS

Granule 1 is Mykon ATC (available from the applicant company) formed from 90-94% TAED carboxymethyl cellulose binder and no more than 2% water and has particle size 95% in the range 0.2 to 1.6 mm.

Granule 2 is Mykon ASD formed from 83 TO 87% TAED, CMC binder and 2.5 to 3.5% methylene phosphonic acid

sequestrant and no more than 2.5% water having particle size 95% in the range 0.2 to 1.6 mm.

The temperature during the reaction was 40°C

Example 8

Storage Stability of Compositions Containing Surfactants

The following compositions were formulated by blending the ingredients in particulate form and storing them in a closed container at ambient temperature. The amount of available oxygen after 12 weeks of storage was determined by standard Avox titration. The percentage loss of available oxygen is reported in the following table.

TABLE 15

Example No.	8.1	8.2
Linear alkyl benzene sulphonate	9%	9%
TAED	3%	3%
Coconut diethanolamide	3%	3%
STPP	20%	20%
C_{13-15} alcohol-7ethoxylate	3.4%	3.4%
Citric Acid	6%	10%
Sodium perborate monohydrate	5%	5%
Sodium Sulphate	to 100%	to 100%
Loss of Avox	6.2%	13.4%

Example 9

Oxidising Agent Concentration for Various Activators at pH 6.3

Mixtures comprising 2.58 g sodium perborate monohydrate, 1.58 g sodium bicarbonate and 2.1 g sodium dihydrogen orthophosphate and 1.88 g of activator, and dissolved into 2 litres of water. The concentration of strong oxidising agent in the solution generated was measured after various periods of time using the iodometric titration mentioned above. The results are given in the following table.

TABLE 16

	Amount of oxidising agent for different activators	
Time	TAE	TAED
5 min	0.45	.6
15 min	0.25	1.7
30 min	0.4	3.6
45 min	0.4	5.1
1 hr	0.35	6.3
1 day	0.4	10.6

These results show that TAED gives excellent long term release of strong oxidising agent, continuing to increase even after one hour.

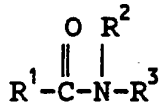
Example 10

A solution of Flash liquid and a similar solution, but with an added amount of bleach booster mixture formed from TAED (at 1.88 g/ℓ), sodium perborate monohydrate (at 2.58 g/ℓ) and citric acid in an amount to give a final pH of 6.5, were compared for their performance in bleaching tea stains. The solutions were applied with a brush to half a stained tile and then either dipped in water or wiped with a cloth to remove the liquid. The whiteness was then recorded as described above. The ΔW values for Flash alone, removed by wiping and dipping, were 4.0 and 9.7, respectively. The ΔW values for the boosted Flash were 4.8 and 13.5 respectively.

CLAIMS

1. A process in which a peroxygen source is reacted with an activator compound which is an N-acyl compound having at least two carbon atoms in the acyl group in a first step in aqueous solution under acidic conditions to form an oxidising product, which is a stronger oxidising agent than the peroxygen source.

2. A process in which a peroxygen source is reacted with an activator compound of the formula I



I

in which R^1 is an alkyl, aralkyl, alkaryl or aryl group, any of which groups has up to 24 carbon atoms and may be substituted or unsubstituted, and $-NR^2R^3$ is a leaving group in which R^2 and R^3 are independently selected from H, C_{1-24}-alkyl, -aralkyl, alkaryl or -aryl groups, and carbonyl-containing moieties having at least 2 carbon atoms in which the carbonyl group is joined to the nitrogen atom in the formula I, in which R^2 and R^3 can be joined together as a cyclic group and/or R^1 can be joined to either R^2 or R^3 to form a cyclic group in a first step in aqueous solution under acidic conditions to form a stronger oxidising agent than the peroxygen source.

3. A process according to claim 2 in which R^1 is an aliphatic group, preferably a C_{1-18} alkyl group, or is an aryl group.

4. A process according to any preceding claim in which the product containing stronger bleaching species is subsequently used as a bleaching and/or disinfecting agent in an aqueous environment at a pH of less than 7.

5. A process according to any preceding claim in which the product of the first step is subsequently used as an oxidising agent in an oxidising step which is carried out without removal of any by-products from the first step.

6. A process according to any preceding claim in which the peroxygen source is selected from hydrogen peroxide, organic peroxides and inorganic persalts.

7. A process according to any preceding claim in which the pH in the first step is less than 7.0 at the beginning of the reaction, preferably less than 6.5 at the beginning of the reaction, and is preferably more than 2.0, more preferably more than 5.0.

8. A process according to any preceding claim in which the concentration of the peroxygen source in the reaction mixture of the first step is less than 10M, preferably less than 5M, more preferably less than 2M, and is preferably at least 0.01M, even more preferably less than 1M and at least 0.05M, especially at least 0.1M.

9. A process according to any preceding claim in which the temperature in the first step of the reaction is in the range 0 to 95°, preferably at least 20°C and up to 80°C, more preferably up to 60°C.

10. Use of a composite product comprising a peroxygen source and an N-acyl activator compound and, if necessary, a component capable of rendering an aqueous solution of the peroxygen source and activator compound acidic to form the reactant mixture for the first step of a process according to any preceding claim, by adding the product to water.

11. Use according to claim 10 in which in the product the activator compound is present in an amount sufficient to provide 0.1 to 5 equivalents acyl groups per mole peroxygen source preferably up to 1.0 equivalents.

12. A use according to claim 10 or 11 in which the acidifying component is present in the product in an amount such that when the components of the product are dissolved in aqueous solution with the peroxygen source being at a concentration in the range 0.01 to 10M (preferably in the range 0.1 to 1.0M) the pH is less than 6.5.

13. A use according to any of claims 10 to 12 in which the activator compound is as defined in claim 2 or claim 3.

14. A use according to any of claims 10 to 13 in which the peroxygen source is selected from hydrogen peroxide, organic peroxides and inorganic persalts.

15. A use according to any of claims 11 to 15 which includes a surfactant.

16. Use according to any of claims 10 to 15 in which the aqueous product is used as an oxidising agent, preferably as a bleaching and/or disinfecting agent.

17. A product containing in the same composition a peroxygen source, an N-acyl activator compound, a surfactant and, if necessary, an acidifying component, such that the product dissolves into water to form an acidic solution.

18. Use of an aqueous solution of a product according to claim 17 as an oxidising agent, preferably as a bleaching and/or disinfecting agent.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 94/00229

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C11D3/39 D06L3/02 C07C409/24 C07C409/26 C07C409/30
D21C9/16 A61L2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C11D D06L C07C D21C A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 551 087 (O. SCHMIDT) 29 December 1970 cited in the application see the whole document	1,2,4-9, 16
A	US,A,2 898 181 (K. DITHMAR ET AL.) 4 August 1959 see the whole document	1-3,5,6
A	EP,A,0 396 287 (THE CLOROX CO.) 7 November 1990 see page 6, line 10 - page 11, line 19; claims	1,10-12, 14-18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 May 1994	02. 06. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serbetsoglou, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/GB 94/00229

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3551087	29-12-70	BE-A-	666517	07-01-66
		CH-B-	450343	
		CH-B-	479750	15-10-69
		CH-A-	880165	
		DE-B-	1269991	
		DE-B-	1269993	
		DE-A-	1469608	19-12-68
		DE-A-	1469609	27-03-69
		FR-A-	1462230	
		GB-A-	1064534	
		NL-A-	6508903	11-01-66
		NL-A-	6916024	26-01-70
		US-A-	3374177	
US-A-2898181		DE-B-	1010048	
EP-A-0396287	07-11-90	CA-A-	2015729	04-11-90
		JP-A-	3007800	14-01-91