P/00/001 28/8/91
Section 29

AUSTRALIA 649496

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

I/We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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[54] Invention Title: STABLE SOLID ACETYL PEROXYBORATE COMPOUNDS

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BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P40 38 202.8	Germany	DE	30 November, 1990.

Basic Applicants: PEROXID-CHEMIE GmbH

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Ian A Scott

17 March, 1994.

Registered Patent Attorney

P/00/0080 12/11/91
Section 29 (1)
Regulation 3.1 (2)

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NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **PEROXID-CHEMIE GmbH** of Dr.-Gustav-Adolf Strasse 3, D-8023 Höllriegelskreuth, Federal Republic of Germany, being the applicant in respect of Application No. 88246/91 state the following:

The Person nominated for the grant of the patent has entitlement to the application by assignment from PEROXID-CHEMIE GmbH entitled in turn by employment contract from the inventors.

The Person nominated for the grant of the patent has entitlement from the applicant of the basic application listed on the patent request form by way of assignment.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

PEROXID-CHEMIE GmbH
By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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17 March, 1994.

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STABLE SOLID ACETYL PEROXYBORATE COMPOUNDS

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(57) Claim

1. A solid acetyl peroxyborate compound characterised by an active oxygen content of 2 to 8% by weight and by a content of peracetic acid, capable of being liberated on dissolution of the acetyl peroxyborate compound in water, of at least 10% by weight and a content of hydrogen peroxide of less than 4% by weight.

10. A washing, cleaning, bleaching agent and/or disinfectant composition containing an acetyl peroxyborate compound according to any preceding claim as an active oxygen-generating component.

13. A process for the production of a solid acetyl peroxyborate compound according to claim 1, comprising:

a) reacting a solid boron oxygen compound with acetic acid and hydrogen peroxide, and/or

b) reacting a solid boron oxygen compound with a solution of peracetic acid in acetic acid, and/or

c) reacting a solid boron oxygen compound containing peroxygen with acetic acid,

if necessary with an addition of acetic anhydride and, according to process variants a) and b) if necessary with an addition of alkaline sodium salt, thereby to form a viscous solution, suspension or paste containing the acetyl peroxyborate; and then drying the acetyl peroxyborate thus formed.

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Regulation 3.2(2)

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: STABLE SOLID ACETYL PEROXYBORATE COMPOUNDS

The following statement is a full description of this invention, including the best method of performing it known to us :-

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The invention relates to new, stable, solid acetyl peroxyborate compounds, to a process for the manufacture thereof, and to compositions which contain these acetyl peroxyborate compounds.

Both inorganic and organic active oxygen compounds are used in detergents, bleaching agents and cleaning agents, in particular those for textiles, in disinfectants and as oxidising agents. Examples of such active oxygen compounds are perborates, persulphates, and mono- and diperoxycarboxylic acids, and in particular, those perborate/activator combinations from which peracetic acid is usually formed in situ.

The peroxycarboxylic acids such as e.g. diperoxydodecanedioic acid (DPDDA) or peracetic acid and perborate/activator combinations such as perborate/tetraacetylethylenediamine (TAED) systems are characterised, in comparison with pure inorganic percompounds such as perborate, by their low effective temperature and their high bleaching and disinfectant power. Also, it is well known according to the state of the art that perborates and peroxycarboxylic acids can be used as oxidising agents in chemical synthesis for the oxidation of organic compounds.

The use of suitable peroxycarboxylic acids for the above-mentioned applications is therefore increasingly desirable. Although progress has already been achieved in the application of peroxycarboxylic acids by the development of peroxycarboxylic acids and/or combinations of perborates and activators forming peroxycarboxylic acids, disadvantages remain to be eliminated.

For many applications, peroxycarboxylic acids that are solid at room temperature are generally the only ones suitable, i.e. fairly long-chain aliphatic peroxycarboxylic acids such as DPDDA which, however, has a poor solubility in water. In addition, peroxycarboxylic acids are thermally and mechanically sensitive in the pure or highly concentrated states and solid peroxycarboxylic acids must therefore be stabilised by suitable desensitising agents, e.g. hydrate-forming inorganic salts such as sodium sulphate. A disadvantage in this connection is that the stability of the desensitised solid peroxycarboxylic acids is considerably influenced by the type and method of peroxycarboxylic acid production and by the desensitisation. In addition,

long-chain peroxycarboxylic acids can be very detrimental to the environment because of the long hydrocarbon chain.

In comparison, peracetic acid, being a short-chain peroxycarboxylic acid with only backbone C atoms, is safe for the environment and characterised by a good solubility in water. However, disadvantages of peracetic acid are that it is liquid at ambient temperature and, in addition, can be produced only as a solution of peracetic acid in acetic acid and not in the pure state. As a result, the possibilities for using peracetic acid as such are limited. To eliminate this disadvantage, activators such as tetraacetylethylenediamine (TAED), have therefore been developed which are capable of forming peracetic acid in situ in the presence of persalts such as perborate. In this case, however, it is a disadvantage that H_2O_2 has to be first formed from the persalt, which liberates the peracetic acid only subsequently by reaction with the activator. Furthermore, the formation of peracetic acid can be negatively affected by the premature decomposition of the hydrogen peroxide formed in situ. In order to be able to better utilise the advantages of peracetic acid there is therefore a need for a simple, stable, non-deliquescent active oxygen compound with an oxidising and/or bleaching effect, which is based on short-chain acetic acid.

The task facing us therefore consisted of developing chemically and physically stable compounds which are safe to handle, which contain active oxygen and which liberate peracetic acid with its high oxidising, bleaching and disinfectant effect during application and which consequently can be used as active oxygen component in detergents, bleaching and cleaning agents and disinfectants and/or as an oxidising agent. It should, moreover, be possible to produce the compounds in a simple manner.

In accordance with the present invention, there are provided solid acetyl peroxyborate compounds which are characterised by an active oxygen content of 2% to 8% by weight and by a content of peracetic acid liberated on dissolution of the acetyl peroxyborate compound in water of at least 10%, preferably of 10% to 30%, by weight and of hydrogen peroxide of less than 4% by weight.

The acetyl peroxyborate compounds according to the invention are colourless, solid compounds and are characterised by a favourable active oxygen stability. Moreover, they are chemically and physically stable during storage and handling at the usual temperatures, this being a substantial advantage from

the safety point of view particularly with respect to production, processing and application. The compounds according to the invention also have high decomposition temperatures and have proved to be mechanically and/or thermally non-critical both in the drop hammer test (>5 mkg) and in the steel cartridge test (<1 mm/Koenen test). The compounds are consequently not sensitive to impact and/or not explosive. It has thus been possible for the first time to combine peracetic acid in a stable solid form from which it can be easily liberated in a simple manner during application in an aqueous medium.

The solid acetyl peroxyborate compounds according to the invention are readily soluble in water and liberate peracetic acid immediately and directly on dissolution in water, but only a relatively little hydrogen peroxide, less than 4% by weight. Particularly advantageous acetyl peroxyborate compounds according to the invention are characterised in that the content of hydrogen peroxide that can be liberated on dissolution of the acetyl peroxy compound in water is less than 3% by weight, preferably less than 1.5% by weight. The peracetic acid content that can be liberated from the acetyl peroxyborate compounds according to the invention is at least 10% by weight, in particular 10% to 30% by weight. Preferred acetyl peroxyborate compounds according to the invention are characterised in that the content of peracetic acid that can be liberated on dissolution of the acetyl peroxyborate compound in water is 20% to 30% by weight.

Although no accurate molecular structure can be determined for the acetyl peroxyborates according to the invention, the compounds according to the invention, on the basis of their chemical origin and/or manufacture, as well as on the basis of their properties, can be defined as being active oxygen-containing compounds based on acetic acid and boron-oxygen compounds. The "acetyl peroxyborates" consequently contain structural elements which are derived from the starting products used in the manufacture, namely acetyl groups, active oxygen and borate structures $\left(-\overset{|}{B}-O-,\ -\overset{|}{B}-O-\right)$. The acetyl groups originate from the basic acetic acid and/or peracetic acid. The active oxygen originates from the basic active oxygen carrier, e.g. H_2O_2, perborate, peracetic acid. The borate structures present in the compounds according to the invention are formed during the formation of the compounds from the basic boron oxygen compounds, but may undergo transformation during this formation so that they need not, in terms of their structure and arrangement, correspond to

the basic boron oxygen compounds. As a result of the content of peracetic acid which can be liberated on dissolution of the solid compound in water, which peracetic acid is presumably at least partly structurally pre-formed in the compounds, the compounds according to the invention can also be considered as a solid peracetic acid derivative (compound splitting off peracetic acid) and/or as a "solid peracetic acid".

The acetyl peroxyborate compounds according to the invention differ substantially from the starting compounds by their chemical and physical properties. As regards the physical properties of the acetyl peroxyborate compounds according to the invention, it must be emphasised on the one hand that they exhibit characteristic IR bands in the IR spectrum in the region of approximately 1650 to 1670cm^{-1} and in the region of approximately 1740 to 1755 cm^{-1} (measured in potassium bromide and/or potassium chloride). Products free from active oxygen obtained from the conversion of boron oxygen compounds (free from active oxygen, e.g. borax) with acetic acid, in contrast exhibit no IR bands in these regions but merely at approximately 1580 cm^{-1}. In addition, they exhibit a characteristic ^{13}C-NMR band in the NMR spectrum (^{13}C-CP/MAS-NMR, solid body spectroscopy: CP - cross polarisation, MAS - magic angle spinning) in the region of 18 to 19 ppm, preferably at approximately 18.5 ppm (measured against tetramethylsilane (TMS) as external standard). According to differential scanning calorimetry, the compounds according to the invention exhibit a characteristic course of the differential calorimetry diagram, the course being endothermic at approximately 135° to 140°C and changing into an exothermic course with an exothermic peak-maximum in the region of approximately 170° to 185°C. As shown by the high decomposition temperature, the compounds according to the invention have a low temperature sensitivity and are consequently characterised by a high thermal stability. Their thermal stability exceeds the stability of the persalts which are known as such, such as sodium percarbonate, sodium perborate monohydrate or sodium perborate tetrahydrate, whose exothermic decomposition peak in the differential calorimetry diagram is at temperatures of 140° to 160°C, and the stability of the peroxycarboxylic acids known as such, such as DPDDA whose exothermic decomposition peak in the differential calorimetry diagram is at temperatures as low as approximately 130°C.

By means of the solid acetyl peroxyborate compounds according to the

invention there is made available for the first time peracetic acid in an application form which is solid at standard ambient conditions, and with an excellent stability and in a favourable form for application. This solid application form of peracetic acid can be used advantageously in detergent, cleaning agent, bleaching agent and disinfectant compositions and as an oxidising agent in organic synthesis. Consequently, the invention provides also detergent, cleaning agent, bleaching agent and disinfectant compositions and oxidising agents for organic synthesis, which contain an acetyl peroxyborate compound according to the invention.

The acetyl peroxyborate compounds according to the invention can be used particularly advantageously as compounds giving off peracetic acid in solid bleaching agent and disinfectant compositions. In a preferred embodiment, the invention consequently relates to solid bleaching agent and disinfectant compositions which contain a peroxyborate compound according to the invention; in this connection, such compositions are particularly advantageous which contain the acetyl peroxyborate compounds according to the invention in the form of powders or granular products in a sachet, or in the form of tablets fused into a film. The acetyl peroxyborate compounds according to the invention can, for example, be used advantageously for dry bleach and as a solid disinfectant that is easy to meter and adjust to the desired concentration during application in aqueous solution.

The use of the acetyl peroxyborate compounds according to the invention in the form of a powder, granular product etc. in a sachet or in the form of a tablet fused into a film is particularly advantageous where aqueous solutions with a defined peracetic acid content are to be prepared by the user. Previously, for example, it has been necessary, when preparing such aqueous peracetic acid disinfectant solutions, to measure out a concentrated, highly corrosive peracetic acid/acetic acid solution with a pungent odour during dosage and to dilute it to the desired concentration by means of water, an operation requiring special safety measures and specially trained personnel. In the case of the compounds according to the invention provided in a sachet and/or as a tablet fused into film, the preparation of aqueous disinfectant solutions and/or the necessary dosage of the disinfectant can take place in a simple manner in that the content of a sachet or the tablet merely need to be introduced into a predetermined amount of water. The preparation and

application of such disinfectant solutions is thus simple to carry out by the person executing the operation, convenient and, moreover, fairly safe.

The invention also relates to a process for the production of the solid acetyl peroxyborate compounds according to the invention, which is characterised in that:

a) a solid boron-oxygen compound is reacted with acetic acid and hydrogen peroxide, and/or

b) a solid boron-oxygen compound is reacted with a solution of peracetic acid in acetic acid, and/or

c) a solid peroxygen-containing boron-oxygen compound is reacted with acetic acid,

if necessary with an addition of acetic anhydride and, according to process variants a) and b) if necessary with an addition of alkaline sodium salt, to give a viscous solution, suspension or paste; and the acetyl peroxyborate compound thus formed is dried.

The acetyl peroxyborate compounds according to the invention can be produced according to the above-mentioned three process variants a) to c) in a simple way by mixing and conversion of the reactants concerned and the optional additives using standard equipment (e.g. mixers, dryers etc.). Appropriately, the reaction is carried out according to these process variants at temperatures of up to 60°C, preferably at temperatures of 30° to 45°C.

The quantities of the reactants used are advantageously adjusted to each other in the three process variants a) to c) as follows:

a) the molar ratio of boron to the acetyl groups and to hydrogen peroxide is 1:(1 to 5):(0.2 to 2),

b) the molar ratio of boron to peracetic acid is 1:(0.2 to 2), preferably 1:(0.5 to 1), and

c) the molar ratio of boron/oxygen compound containing peroxygen to the acetyl groups is 1:(1 to 10), preferably 1:(2 to 6).

According to process variants a) and b), solid boron-oxygen compounds known as such can be used as the starting products. Examples of these are in particular boric acid, boron oxide (B_2O_3) or polyborates such as e.g. borax ($Na_2B_4O_7$ with up to 10 waters of hydration), sodium metaborate and sodium metaborate hydrate. Boron oxygen compounds with a low content of or free from water of hydration, such as boron oxide, and polyborates with a low content of

or free from water of hydration such as borax with up to 3 waters of hydration (e.g. borax dihydrate or borax trihydrate) or borax anhydride ($Na_2B_4O_7$), are advantageous. Boron oxide which gives an excellent reaction (e.g. with an addition of sodium acetate as alkaline sodium salt) and, for economic reasons, the so-called borax B ($Na_2B_4O_7$ with approximately 2 to 3 waters of hydration) and/or the so-called borax C ($Na_2B_4O_7$ with approximately 0 to 1 water of hydration) are preferred. Borax types B and C can be prepared from the so-called borax A (borax decahydrate having the formula $Na_2B_4O_7.10H_2O$) by dehydration processes known as such. Borax B, for example, is obtained from borax A by 2 hours drying at 150°C in a circulating air oven. To obtain borax C, the Borax B thus obtained is additionally dried for 1 hour at 400°C.

According to variant a), the acetyl peroxyborate product according to the invention is formed directly from simple starting products, e.g. from boron oxygen compound, acetic acid and hydrogen peroxide as well as, if necessary, acetic anhydride and, if necessary, alkaline sodium salt via peroxygen-containing boron oxygen compounds (perborates) formed as intermediate products and/or peracetic acid formed as intermediate product. To form the acetyl peroxyborate product according to the invention using process variant b), the boron oxygen compound used is reacted with a pre-formed peracetic acid (as peracetic acid solution in acetic acid), whereby the crystalline modifications of the boron oxygen compounds used, in particular, are highly advantageous.

Solid peroxygen-containing boron oxygen compounds known as such (e.g. perborates or peroxyborates, superoxidised perborates) can be used as starting products for process variant c). In particular, perborates which are free from or have a low content of water of hydration and with a molar ratio of Na:B of 0.3:1 to 1:1 are advantageously used. Most preferably the perborates which are used are sodium perborate monohydrate and sodium perborate with a molar ratio of Na:B of 0.4:1 to 0.7:1. If perborates are used with a non-conventional Na:B molar ratio of 0.45:1 to 0.65:1, advantageous acetyl peroxyborate products are obtained with a high content of liberatable peracetic acid.

The conversion for the production of the acetyl peroxyborate compounds according to the invention takes place in a fairly simple manner by mixing the starting compounds and causing them to react. If required, acetic anhydride is added, in particular to collect water; or an alkaline sodium salt is added, if desired, in order to adjust the required Na:B molar ratio. If boron oxide

and/or boric acid is used exclusively as boron oxygen compounds, an alkaline sodium salt is added in every case to adjust the desired Na:B molar ratio. Suitable alkaline sodium salts are sodium hydroxide, sodium carbonate, sodium acetate, sodium phosphates and/or other alkaline sodium salts; sodium carbonate or sodium acetate are particularly advantageous. During the reaction, a viscous solution, suspension or paste is formed which is agitated or kneaded with heating or, if applicable, with a spontaneous increase in temperature. The time which is appropriate or required for the conversion can vary depending on the process variant. According to process variant c), the conversion time can be as much as 100 hours, preferably 5 to 30 hours. According to process variant a) the conversion time can be 50 hours, preferably 2 to 20 hours. According to process variant b) the conversion time can range from very short periods up to 10 hours, but preferably up to 5 hours; in the most advantageous case, the reaction mixture can be dried directly after mixing of the starting products to remove an excess in particular of acetic anhydride and/or glacial acetic acid in order to obtain the acetyl peroxyborate compound.

For reactions according to variants a) to c), it has, moreover, proved advantageous particularly with a view to a high content of liberatable peracetic acid and good stability of the product, to add as little water as possible during the reaction. When selecting the starting products, care should therefore be taken to ensure that as little water as possible is introduced with them into the reaction. Not only boron oxygen compounds free from or with a low content of water of hydration and containing oxygen or peroxygen are preferred, as mentioned above, but also the other starting components such as, in particular, acetic acid, hydrogen peroxide (e.g. with an H_2O_2 content of $>50\%$ by weight) and the solutions of peracetic acid in acetic acid, are used in their low water content forms. According to embodiments of process variant a) which are particularly preferred, a hydrogen peroxide solution with an H_2O_2 content of at least 70% by weight is therefore used in particular. In process variant b), a solution of peracetic acid in acetic acid, containing as little water as possible, is used in particular; for this reason, those peracetic acid solutions are preferred in particular which are prepared from acetic acid and/or acetic anhydride and hydrogen peroxide with an H_2O_2 content of at least 50% by weight, preferably at least 70% by weight. According to the highly advantageous process variant b) it is recommended to

use, in particular pre-formed peracetic acid solutions with a particularly low water content e.g. peracetic acid solutions with an approximate composition of approximately 21.5% by weight peracetic, 0.5% by weight hydrogen peroxide, 71.5% by weight acetic acid and maximum approximately 6.5% water. If necessary, the water content can be reduced by a further addition of acetic anhydride.

According to appropriate embodiments of the invention, stabilisers commonly employed for percompounds are used for the production of the acetyl perborate compounds according to the invention, or they are already present in the starting products used. The stabilisers can also be used after the conversion and before the drying step. Phosphates such a metaphosphate, organic stabilisers such as quinolinic acid, salicylic acid or dipicolinic acid (DPA), chelating agents such as 8-oxyquinoline or ethylene diamine tetraacetic acid (EDTA), phosphonic acid derivatives such as methylene and/or aminomethylene phosphonic acids or the salts thereof as well as small quantities of the usual wetting agents are suitable for use as stabilisers. Particularly suitable stabilisers, especially with a view to the long term stability of the products according to the invention are e.g. 1-hydroxyethane-1,1-diphosphonic acid, ethylenediamine tetramethylene phosphonic acid, diethylenetriamine-pentamethylene phosphonic acid and the salts thereof. Such stabilisers can be incorporated into the product according to the invention in the usual concentration of 0.1 to 10g/kg. If the stabilisers are introduced during the preparation of the acetyl peroxyborate compounds according to the invention, this can preferably take place via the hydrogen peroxide solution or the peracetic acid solution used. In particular, the stabilisers are used in quantities such as are required to be present in the products later on.

The conversion of the starting products to the acetyl peroxyborate compounds according to the invention can be carried out in conventional equipment. The reactions can, for example, take place with agitation in stirred glass, enamel or polyethylene vessels. Initially free-flowing solutions or suspensions are obtained which gradually become more viscous or paste-like and, in this still pumpable state, can be transferred into drying equipment to remove the water and excess acetic acid. The conversion can also be carried out highly advantageously in high-speed vacuum intensive mixers in which the subsequent drying operation can also take place. In this way, round

granular products with a grain size of 1 to 3 mm are obtained, the fines which may be formed being removed by subsequent sieving and, if necessary passed to further granulation operations. Advantageously, turbulence mixers (mixing mills with adjustable grain size) can also be used which permit better control of the grain size of the product.

In another highly advantageous embodiment of the process of the invention leading to particularly advantageous products, before the final drying, the acetyl peroxyborate compounds obtained in paste form or following intermediate drying are washed with an inert solvent. Preferred solvent for this operation are in particular low alcohols such as C1- to C3-alcohols (methanol, ethanol, propanol, isopropanol) or esters of these alcohols with acetic acid. A particularly preferred low alcohol is ethanol and a particularly preferred ester is acetic acid ethyl ester. Industrial solvents which need not be completely anhydrous can also be used for washing.

Following the reaction or after intermediate drying and washing with inert solvent if this expedient is employed, water and the excess acetic acid used or, if necessary residues of the inert solvent used for the washing, are removed from the reaction mixture which generally is obtained in the form of a viscous solution, suspension or paste. For this drying step convention procedures e.g. air drying, vacuum drying, roller drying, spray drying or fluid bed drying, for example, may be used.

Drying is carried out under conditions known to be suitable for peroxygen-containing compounds, the conditions to be maintained, in particular the drying temperature, depending on the drying process and the residence time of the product concerned.

Spray drying processes, for example, provide a careful and rapid method for the preparation of the product, which appropriately is also suitable for producing fairly large quantities of product. The viscous solutions or suspensions obtained from the reaction can either be used directly for spray drying or the pastes obtained during the reaction can, if necessary, be spray dried after conversion into a sprayable suspension. The conversion of pastes to sprayable suspensions can take place by adding inert solvents such as those used for the wash process described above, for example by adding acetic acid ethyl ester. Any spray drying process as such can be used. For example, standard spray dryers (SD) or special dryers such as spin-flash dryers which

are also suitable for drying pastes without conversion into a suspension can be used, as well as fluid bed spray dryers (FSD) or fluid bed spray granulators (FSG), the latter two types of equipment permitting, besides drying of the product, also granulation of the product in association with the drying step. The drying temperatures (off-gas temperatures) depend on the residence time of the product but generally are approximately 80° to 130°C, preferably 95° to 115°C, in the case of short residence times in the spray dryer; in the case of longer residence times, e.g. in the fluid bed spray granulator (FSG), the drying temperatures generally are 50° to 90°C.

The acetyl peroxyborates according to the invention can also be dried in another way in a stream of air, e.g. in fluid bed or circulating air dryers. In this case, the drying temperatures generally range from 30° to 80°C and preferably 40° to 60°C. Another possibility consists of vacuum drying, leading in particular to very high yields as regards the content of liberatable peracetic acid in the product. The drying temperatures during vacuum drying are generally 30° to 80°C, preferably 40° to 60°C under a water-jet vacuum or at pressures of approximately 15 to 100 mbar.

It is also possible to combine different drying processes; this can be particularly appropriate if the products are to undergo intermediate drying before washing with inert solvents. The products can thus be initially predried, e.g. by vacuum drying, to a certain level and subsequently, if necessary, washed with inert solvent and finally dried in a stream of air, for example in a fluid bed or a circulating air dryer as indicated. Using special equipment it is moreover possible to carry out both the conversion of the starting products, granulation of the product formed and final and/or intermediate drying as a "single pot process" in a vacuum mixer suitable for granulation, e.g. in an intensive vacuum mixer.

In a very preferred embodiment of process variant b) described above, the reaction of the boron oxygen compound with a pre-formed peracetic acid solution is carried out in specially equipped mixers in such a way that granules of the acetyl peroxyborates are already obtained within short reaction and crystallisation times. This process for the preparation of solid acetyl peroxyborate compounds is characterised in that, in accordance with process variant b), in a mixer which is provided with a rotary mixing tool and comminuting auxiliary mixing tool, with a heat exchange installation for

cooling and heating and with a vacuum installation, at least the comminuting auxiliary mixing tool being characterised by a Froude number $Fr > 1$, preferably $Fr >> 1$,

b1) a pre-formed solution of peracetic acid in acetic acid and a boron oxygen compound having a low water content are reacted with one another in such a way that the temperature does not exceed about 40°C,

b2) seed crystals of acetyl peroxyborate are added and

b3) a paste of acetyl peroxyborate is formed by mixing at temperatures of up to 45°C

b4) a lubricant is optionally added to the paste and the paste is pre-dried under vacuum at a product temperature of up to about 60°C, preferably of 35° to 55°C, until a granular acetyl peroxyborate forms, the comminuting auxiliary mixing tool being switched on for a brief period in the course of this pre-drying, after passing through a break-up stage and at the start of disintegration of the substantially pre-dried paste of acetyl peroxyborate, and subsequently, in step b5), either

b5.1) the pre-dried acetyl peroxyborate is completely post-dried under normal pressure and at a product temperature of up to about 80°C, preferably up to about 60°C, and the desired particle size fraction of the acetyl peroxyborate is then separate off by sieving, or

b5.2) the desired particle size fraction of the acetyl peroxyborate is first separated off from the coarse and/or fine fractions by sieving the pre-dried acetyl peroxyborate, and then only that fraction having the desired particle size is completely post-dried under normal pressure at a product temperature of up to about 80°C, preferably up to about 60°C,

by which means the acetyl peroxyborate is obtained in the form of solid, particulate and flowable granules.

In the case of the above embodiment of process variant b), the reaction of boron oxygen compound with peracetic acid is carried out in specially equipped vacuum mixers, for example turbulent vacuum mixers or intensive vacuum mixers, which have at least one mixing or comminuting tool rotating at high speed,

which is characterised by Froude numbers >1, preferably even by Froude numbers very much greater than 1, a large Froude number being of importance in particular after the break-up phase, described below, for granule formation. The Froude number is a criterion for the movement of material in a compulsory mixer and describes, as classification parameter, the interaction of inertia forces and gravitational forces. The Froude number Fr is therefore used for the characterisation of mixing processes and for the classification of mixer types; it is defined as $Fr=Rw^2/g$, where R = external radius of the mixing element, w = angular velocity and g = acceleration due to gravity. For temperature control during the reaction and drying, the mixer types employed must have a heat exchange installation which permits both cooling and heating. For example, the mixers can be provided with a double casing suitable for cooling and heating. Apart from the rotary tool, which can be designed in the manner of a ploughshare mixer or blade mixer, the mixers used here additionally have mixing aids for comminution which rotate at high speed and which, for example, are designed in the nature of pinned-disc mills. The mixer types employed are thus equally suitable for mixing and comminuting and for rounding as well as for vacuum drying of the product. Therefore, reaction, crystallisation, drying and granulation can be carried out in a single apparatus (one-pot process).

In the reaction according to the above embodiment of process variant b), the peracetic acid solution is reacted in the mixer with a solid boron-oxygen compound in the form of a powder or granules. With this procedure, both the peracetic acid and the boron-oxygen compound are used in a form in which the water content is reduced, it being possible easily to lower the water content introduced into the pre-formed peracetic acid solution with the educts by adding acetic anhydride during the preparation of the peracetic acid. To this end, acetic anhydride is added in up to an approximately equimolar amount relative to the water content of the educts, which serve for the preparation of the peracetic acid. Like the pre-formed peracetic acid solution, the boron-oxygen compound used should also be introduced into the reaction mixture in a form having a reduced water content. Therefore, borax hydrates having a low water content are preferred, in particular those borax hydrates which, for example, satisfy the formula $Na_2B_4O_7\ (H_2O)_{0-3}$ and have a boron content of about 17 to 21% by weight; this corresponds to a formal water of hydration content of

0 to 3 mol, the water being bound as structural water in $Na_2B_4O_5(OH)_4$ in the case of contents of less than 2 mol. Borax hydrates having a formal water of hydration content of about 1 to 2 mol are particularly preferred.

It is important for the formation of the acetyl peroxyborate according to the invention in the vacuum mixer in accordance with the above process variant that seed crystals of acetyl peroxyborate are added to the reaction mixture comprising peracetic acid solution and boron oxygen compound in step b2). By this means, the reaction time and the crystallisation time are advantageously shortened. The addition of seed crystals of acetyl peroxyborate in accordance with step b2) can, therefore, take place either during the reaction of the boron-oxygen compound with the peracetic acid solution in accordance with step b1) or once this reaction has taken place. The seed crystals used for b2) can, per se, be any acetyl peroxyborate; for example coarse and/or fine fractions (oversize and/or undersize particles) of acetyl peroxyborate, which in the subsequent process steps can be separated off from the desired particle size fraction of the acetyl peroxyborate by sieving. As a result of the unrestricted recycling of particle size fractions of the acetyl peroxyborate containing oversize and/or undersize particles, an advantageous and complete utilisation of the raw materials employed can be ensured. The amount of seed crystals added depends on the amount of undersize or oversize particles obtained from sieving and has no critical upper limit. Distinct effects on the reaction and crystallisation time are obtained by addition in an amount of from at least about 2% by weight, based on the reaction mixture in step b1). If the amount added is less than 2% by weight, a longer reaction and crystallisation time must be accepted.

In step b3), following the above reaction and addition of seed crystals, a paste of acetyl peroxyborate is formed from the reaction mixture, while mixing at temperatures of up to about 45°C, preferably at temperatures of about 35 to 40°C, by progressive crystallisation. In step b4), the bulk of the solvent and other volatile constituents are removed from this paste by gentle vacuum drying, optionally with the addition of lubricant. The vacuum drying is carried out, for example, under a pressure of about 10 to 100 mbar. During this drying the product temperature is adjusted to about 60°C, preferably to 35° to 55°C. The solvent (acetic acid) can by this means be removed from the acetyl peroxyborate paste under highly product-protecting conditions and

recycled into the preparation of pre-formed peracetic acid solution. In the course of the vacuum drying, the solvent content decreases and the acetyl peroxyborate paste passes into a plastic state, the viscosity of which further increases during vacuum drying. During this procedure, a stage which is critical for granule formation, the break-up stage, is reached after some time, the viscosity of the product then further increasing considerably. The start of this break-up stage can be recognised by the fact that, for example, the electric current consumption of the mixture distinctly increases. In the course of this break-up stage the acetyl peroxyborate changes from the state of a viscous, plastic mass into a solid product state which, however, can still be kneaded by the mixer. At the end of the break-up stage, this solid, but still kneadable state of the acetyl peroxyborate is broken through by the mixer with disintegration of the kneadable paste and formation of an acetyl peroxyborate product which is now crumbly, at which point the process has then gone beyond the break-up stage. Immediately after passing through the break-up stage, that is to say after the break-through, the comminuting auxiliary mixing tool, preferably a pinned-disc mill, must be switched on for a brief period of a few minutes. This period depends on the degree of comminution desired and can be, in particular up to about 10 minutes. The action of the comminuting auxiliary mixing tool is important for granule formation with regard to the particle shape and control of the particle size. In this procedure, the optional addition of lubricant reduces the energy requirement during the break-up stage and facilitates progress through the break-up phase, including comminution.

In step b4) of the present process, it is possible to use any lubricant which is stable to oxidation and is compatible with the educts and products. Suitable lubricants are, for example, metal salts of fatty acids, in particular alkali metal and/or alkaline earth metal salts of relatively long chain saturated fatty acids, which preferably are straight-chain and can contain up to 18 carbon atoms, in particular 16 to 18 carbon atoms. Salts of stearic acid prove particularly advantageous. The above-mentioned metal salts of fatty acids which are preferably used are those of the alkali metals and/or alkaline earth metals of the second and third period of the periodic system of the element, but in particular those of sodium, potassium or magnesium. Magnesium stearate is particularly preferred. In this process, the lubricant, if used, is added at the start of pre-drying in step b4) in an amount of up to 5% by

weight, preferably in an amount of 0.2 to 1% by weight, to the acetylperoxyborate paste obtained in step b3); the amounts indicated here are based on the reaction mixture in step b1).

Following the vacuum pre-drying in accordance with step b4), solid, particulate acetyl peroxyborate granules are obtained which can still contain up to about 10% by weight of volatile constituents, for example acetic acid and/or water. For complete removal of these residual volatile constituents, the granules must be post-dried under more severe drying conditions in a further drying step, since a more extensive drying under vacuum conditions is very time-consuming and does not lead to the required degree of drying. The post-drying has a clear beneficial effect on the stability of the product.

Therefore, the above first drying step, the pre-drying under vacuum in accordance with step b4), is followed in step b5) by a second drying step, in particular, for example, an air drying. In this step, drying of the acetyl peroxyborate product from step b4) is carried out under normal pressure and at product temperatures of up to 80°C, but in particular up to about 60°C, until the residual volatile constituents (for example acetic acid and water) have been completely removed form the product. The post-drying in process step b5) can be carried out in two variants. In a first variant b5.1) the acetyl peroxyborate product from the vacuum drying in step b4) is first completely post-dried, for example by air drying, and only then is the desired particle size fraction of the acetyl peroxyborate separated off by sieving. In a second variant b5.2), the desired particle size fraction of the acetyl peroxyborate granules is first separated off by sieving the acetyl peroxyborate product pre-dried in step b4) and then only this fraction having the desired particle size is completely post-dried, for example by air drying. The fractions of the acetyl peroxyborate granules which contain oversize and/or undersize particles (coarse fractions and fine fractions) which are separated off can subsequently advantageously be recycled into the preparation process as crystallisation seeds for step b2). The air drying can be carried out, for example, by the processes which are conventional per se in the prior art, preferably by drying in a fluidised bed. In process variant b5.1), the final drying can optionally also be carried out in the vacuum mixer, provided that the latter is additionally provided with installations for the supply of dry air and the removal of waste air.

The process according to the invention for the preparation of acetyl peroxyborates in accordance with process steps b1) to b5) has particular advantages. In particular, this process enables the reaction time for formation of the acetyl peroxyborate to be considerably shortened compared with the other process variants. The two-step drying enables volatile constituents such as acetic acid and water to be completely removed from the reaction product under product-protecting conditions. With this procedure, the bulk of the volatile constituents are first removed under the mild conditions of a vacuum drying, whilst only a small proportion of up to about 10% by weight of volatile constituents is then completely removed under the more severe conditions of the second drying step. By this means, very stable products which are stable on storage are obtained. Furthermore, the product is already obtained in granule form, as a result of which further granule-building operations are superfluous. The product can thus be supplied for further use directly, if appropriate after coating with a coating.

Using the processes and process variants described above, acetyl peroxyborate compounds according to the invention can thus be produced advantageously. As a rule the compounds according to the invention are obtained in the form of colourless powders or granules and can then be processed further by known measures for the intended application. For example, they can be processed by known granulation or agglomeration processes to appropriate application forms such as, for example, extruded cut sections, pellets, granules, brickettes, tablets or granular products of the desired grain fraction, etc. The granule or agglomerated products can, if necessary, be additionally coated by coating processes known as such. For the preparation of granular products, agglomerates or tablets, auxiliary agents commonly used for this purpose such as binders, slips, agents promoting disintegration, stabilisers etc. can be used. Moreover, the acetyl peroxyborate compound can, for certain applications, be additionally fused into a film, e.g. standard household polyethylene film, for protection against moisture. This is advantageous in particular for bleaching applications (e.g. dry bleach, stain removal salt) or disinfectant applications, since this facilitates obtaining a desired dosage.

Preferred acetyl peroxyborate compounds according to the invention have a number of advantages. As compounds splitting off peracetic acid, for example,

they exhibit an excellent bleach performance even, in preferred cases, vis-a-vis difficult stains such as red wine or tea, their bleaching performance being not only equal to that of DPDDA systems but considerably exceeding that of conventional perborate/TAED systems. This high bleach performance is also achieved in liquid detergents and in comparison with common stain removal salts (percabonate/TAED systems). Moreover, the bleaching agent, namely peracetic acid, becomes more rapidly available from the compounds according to the invention than from the standard perborate/TAED bleach systems. Also, the acetyl peroxyborate compounds according to the invention have advantages for use as disinfectants. Thus, preferred compounds according to the invention correspond in terms of their microbicidal effect to peracetic acid but are more advantageous compared with peracetic acid because of their solid form. The compounds according to the invention can thus be apportioned easily for this application e.g. in the form of tablets or packaged portions of granular material.

Granules of the acetyl peroxyborate compounds according to the invention also have advantages during use as stain removal or bleaching agents in portion-form (e.g. fused or deep-drawn into film, portion dishes closed with laminated film) particularly in the case of joint use together with liquid detergents. When used together with liquid detergents, these bleaching agents can then be added separately in the form of portions to the bleaching agent-free liquid detergent in the wash process.

The following examples are to illustrate the invention without restricting its scope. The abbreviations used have the following meaning: PAA - peracetic acid; IR - infra-red spectroscopy; NMR - nuclear resonance spectroscopy; CP/MAS - cross polarisation/magic angle spinning; DSC - differential scanning calorimetry;

Borax B: $Na_2B_4O_7.(H_2O)_{2-3}$ obtained from borax A - $Na_2B_4O_7.10H_2O$ by 2 hours drying at 150°C in the circulating air oven.

Borax C: $Na_2B_4O_7.(H_2O)_0$ - 1 obtained from borax B by additional 1 - hour drying at 400°C.

PBS-1: Sodium perborate monohydrate; Oa: active oxygen; DPDDA: diperoxydidecanedioic acid; TAED: tetraacetylethylene diamine; PBS-4: sodium perborate tetrahydrate; PCS: sodium percarbonate.

Example 1:

10 g sodium perborate monohydrate (15% by weight active oxygen) were reacted with 30 g acetic acid (96% by weight) for 20 hours at 35°C in a stirred vessel with stirring to the consistency of an homogeneous paste and subsequently dried for 2 hours at 40°C under vacuum in a water-jet pump (molar ratio of the reactants: 1:5).

15 g of an acetyl peroxyborate were obtained as dry product in the form of a white powder with the following composition and properties:

Active oxygen content: 3.5% by weight
Content of PAA liberatable in water: 16% by weight
Content of H_2O_2 liberatable in water: 0.2% by weight.

Example 2

40 g of a sodium peroxyborate with a molar ratio of sodium to boron to active oxygen of 0.6:1:1.1 were reacted with 120 g acetic acid (96% by weight) with stirring in the course of 20 hours at 30°C to form a paste. The molar ratio of Na:B:Oa:acetic acid in the reaction mixture was subsequently 0.6:1:1.1:4. Subsequently, drying was carried out at 40°C under vacuum.

69 g of an acetyl peroxyborate with the following composition and properties was obtained as the dried product.

Active oxygen content: 6.4% by weight
Content of PAA liberatable in water: 25% by weight
Content of H_2O_2 liberatable in water: 2.4% by weight
DSC: endothermic peak (maximum) at approx. 160°C
exothermic peak (maximum) at approx. 178°C

Example 3

30 g borax C (20.6% by weight boron) were reacted with 137 g acetic acid (99.8% by weight) and 23 g hydrogen peroxide (85% by weight) in a molar ratio of Na:B:Oa:acetic acid of 0.5:1:0.97:3.92 with stirring for 15 hours at 30°C to form a paste. Subsequently, drying was carried out at 40°C under a water-jet vacuum.

73 g of an acetyl peroxyborate with the following composition and properties were obtained as dried product:

Active oxygen content: 6.1% by weight
Content of PAA liberatable in water: 26.1% by weight
Content of H_2O_2 liberatable in water: 1.2% by weight
IR (KBr, cm^{-1}): 1748: 1660
^{13}C-CP/MAS-NMR: 18.6 ppm
DSC: endothermic peak (maximum) at approx. 150°C
exothermic peak (maximum) at approx. 180°C
(additional endothermic peak at approx. 215°C)

Example 4

a) Preformed peracetic acid was prepared. For this purpose, 170 g acetic acid (99.8% by weight) and 30 g 85% by weight hydrogen peroxide were stirred with an addition of 1 g concentrated sulphuric acid for 1.5 hours at 35°C. 200 g of a preformed peracetic acid solution with a peracetic acid content of 24.5% by weight and a residual content of free hydrogen peroxide of 1.4% by weight were obtained.

b) 150 g of the peracetic acid solution obtained under a) were reacted with 24 g borax C (20.9% by weight boron) corresponding to a molar ratio of Na:B:PAA of 0.5:1:1 to form a homogeneous suspension and subsequently dried at 40°C under a water-jet vacuum.

55 g of an acetyl peroxyborate in the form of a powder with the following composition and properties were obtained as the dried product:

Active oxygen content: 6.6% by weight
Content of PAA liberatable in water: 28% by weight
Content of H_2O_2 liberatable in water: 1.6% by weight

Example 5

40 g of a peracetic acid solution prepared as in Example 4a) were reacted with 20 g borax C (20.9% by weight boron) corresponding to a molar ratio of Na:B:PAA of 0.5:1:0.5 in the course of 3 hours at 35°C to form a paste. The paste obtained was washed twice with 50 ml ethanol on a suction filter. Subsequently, drying was carried out for 2.5 hours at 50°C in a circulating air drying cabinet.

An acetyl peroxyborate in the form of an extremely stable white powder with the following composition and properties was obtained as the dried product:

Active oxygen content: 6.1% by weight
Content of PAA liberatable in water: 28% by weight
Content of H_2O_2 liberatable in water: 0.4% by weight
IR (KCl, cm^{-1}): 1748: 1661
^{13}C-CP/MAS-NMR: 18.5 ppm
DSC: endothermic peak (maximum) at approx. 160°C
exothermic peak (maximum) at approx. 172°C

Example 6

Initially, 40 g of a sodium peroxyborate with a molar ratio of sodium to boron of 0.6:1 and a molar ratio of boron to active oxygen of 1:1.1 (active oxygen content 20% by weight) and 120 g acetic acid (96% by weight) were reacted for 20 hours at 30°C with stirring to form a homogeneous paste. The molar ratio of Na:B:Oa:acetic acid in the reaction mixture was thus 0.6:1:1.1:4.2. By adding 100 ml acetic acid ethyl ester, the paste obtained was subsequently converted into a sprayable suspension which was then sprayed in a spray drier at off-gas temperatures of 100 to 105°C.

A dry acetyl peroxyborate with the following composition and properties was obtained as the sprayed product:

Active oxygen content: 6.6% by weight
Content of PAA liberatable in water: 25% by weight
Content of H_2O_2 liberatable in water: 2.8% by weight
DSC: endothermic peak (maximum) at approx. 152°C
exothermic peak (maximum) at approx. 170°C

Example 7

61.4 g of a peracetic acid solution prepared according to example 4a) were reacted with 20 g borax B (16.3% by weight boron; approx. 3 (g?) water of hydration corresponding to borax trihydrate) corresponding to a molar ratio of Na:B:PAA of 0.5:1:0.67 were reacted for 3 hours at 35°C to form a paste. Subsequently, the paste was converted with 150 ml acetic acid ethyl ester to a sprayable suspension which was then sprayed in a spray drier at off-gas temperatures of 100 to 110°C. An acetyl peroxyborate with the following composition and properties was obtained as the sprayed product:

Active oxygen content: 4.6% by weight
Content of PAA liberatable in water: 21.5% by weight
Content of H_2O_2 liberatable in water: 0.1% by weight
DSC: endothermic peak (maximum) at approx. 150°C
exothermic peak (maximum) at approx. 175°C

Example 8

10 g borax C (20.8% by weight boron) were added to 30.3 g of a peracetic acid solution prepared according to example 4a) and stirred for 3 hours at 35°C. 100 ml acetic acid ethyl ester were subsequently added to the suspension thus obtained and this was sprayed in a conventional spray drier at off-gas temperatures of 115°C.

A dry acetyl peroxyborate with the following composition and properties was obtained as the sprayed product:

Active oxygen content: 5.7% by weight
Content of PAA liberatable in water: 25% by weight
Content of H_2O_2 liberatable in water: 1% by weight
DSC: endothermic peak (maximum) at approx. 140°C
exothermic peak (maximum) at approx. 170°C

Example 9

a) A mixture was prepared initially from 84% by weight technical grade acetic acid (96% by weight), 15% by weight hydrogen peroxide (85% by weight) and 1 part by weight concentrated sulphuric acid; this was stirred for approximately 1.5 hours at 35°C. Subsequently, acetic anhydride (17 parts by weight based on the total quantity) was added to this mixture and stirring was continued for a further hour at 35°C. The preformed peracetic acid solution thus obtained contained 22% by weight peracetic acid, 71% by weight acetic acid, 0.5% by weight hydrogen peroxide and 6.5% by weight water.

b) The peracetic acid solution prepared above was reacted with borax B (18% by weight boron) with a molar ratio of boron to peracetic acid of 1:0.55 for 3 hours at 40°C. A product with a consistency ranging from a paste to a solid was obtained which, by drying in the rotary evaporator, gave an acetyl peroxyborate with a content of peracetic acid liberatable in water of 28% by weight. The other analytical data corresponded to those of the product detailed in example 4.

Example 10

3290 g of a peracetic acid solution pre-formed according to example 9a) were reacted with 1000 g borax B (18.3% by weight boron) and 35 g 1.1-hydroxyethane diphosphonic acid (60% by weight in H_2O) in an intensive vacuum mixer under normal pressure for 4 hours at 35°C to form a paste. Subsequently, the paste was dried in this mixer under vacuum for 1 hour at 50°C. During this process, the product was granulated to form a granular material with particle sizes of approximately 1 to 3 mm. The granular product produced was subsequently additionally dried for 3 hours at 50°C in the circulating air drying cabinet. A dry free-flowing granular product with the following composition and properties was obtained:

Active oxygen content: 5.6% by weight
Content of PAA liberatable in water: 26% by weight
Content of H_2O_2 liberatable in water: 0.2% by weight
DSC: endothermic peak (maximum) at approx. 167°C
exothermic peak (maximum) at approx. 181°C

Example 11

282 g of a pre-formed peracetic acid with the following composition: 25% by weight PAA and 1.8% by weight H_2O_2 were added to a mixture of 64.4 g boron oxide (B_2O_3) and 76.7 g sodium acetate. A molar ratio of Na:B:PAA of 0.5:1:0.5 was present in the reaction mixture. The reaction temperature was maintained at 35°C. After 1 hour, a paste was obtained which was initially dried for 2 hours at 40°C under a water-jet vacuum and subsequently dried for a further 1 hour at 50°C. The acetyl peroxyborate obtained had a content of PAA liberatable in water of 27% by weight.

Example 12

To investigate the stability, the products obtained in examples 1 to 11 were examined for their stability in the dry state. To determine the stability in the dry state, the samples to be examined were exposed to the conditions detailed in Table 1 and subsequently the loss of active oxygen from the peracetic acid as a result of decomposition was determined.

The determination of the active oxygen content before and after the treatment detailed in Table 1 was carried out by titrimetric methods known as such. Table 1 provides a survey of the conditions and the results obtained.

Table 1 Stability tests, Example 12

Example	Test conditions	Loss of active oxygen in %
a) Open storage in the drying cabinet		
1	60 °C / 4 Weeks	6
2	60 °C / 4 Weeks	5
3	60 °C / 4 Weeks	15
9	60 °C / 5 Weeks	5
9	60 °C / 6 Months	16
b) Short term stability at elevated temperature		
5	100 °C / 1 h	4,4
6	100 °C / 1 h	11
7	100 °C / 1 h	8
8	100 °C / 1 h	10
10	100 °C / 1 h	5
PBS-1* (reference)	100 °C / 1 h	7-10
c) Storage in the closed polyethylene flask		
2	20 °C / 420 days	1[illegible]
5	20 °C / 205 days	9
6	20 °C / 337 days	14
10	20 °C / 120 days	1,8

(* Active oxygen from H_2O_2)

Example 13

The effectiveness of the acetyl peroxyborate compounds according to the invention as a bleaching agent in heavy duty detergents (a) and as a bleaching wash additive (b) was examined by way of test stains used as an example and in comparison with the usual bleaching agent systems.

The wash tests were carried out either in a laboratory facility of the Linitest-type or in a front loader domestic washing machine of the Miele Sensor-Electronik W 784 type commonly available on the market. The wash temperatures were 40°C or 60°C. The fabrics with test stains were washed with an addition of 2 kg white woven towels used as an additional load.

The following commercially available woven fabric sections with tea or red wine contamination covering the entire surface were used as test fabrics:

- test fabric WFK Tea 106; pure cotton test fabric from Wäschereiforschung Krefeld with tea staining;

- test fabric EMPA Red wine 114; pure cotton test fabric from the Swiss Material Testing Institute at St. Gallen (Switzerland) with red wine staining.

In addition, a test fabric prepared in-house was used:

- cotton/polyester test fabric: mixed fabric consisting of cotton and polyester (50/50) with a weight per square metre of 240 g and tea test staining (cotton/PE Tea) or red wine staining (cotton/PE Red wine).

Phosphate-free, zeolite-containing base powder in the form of commercial products available on the market without a source of active oxygen, a commercial grade heavy duty branded detergent containing active oxygen and commercial grade liquid detergents were used as the wash components. The quantities used depended on the manufacturers' dosage recommendations. The bleaching agent according to the invention or, for reference purposes, the bleaching systems commonly used were added to the wash components. The dosage of the compounds according to the invention and the reference substances consisted either of the same quantity by weight (equivalent weight) or of quantities equivalent in term of the active oxygen content used (Oa equivalent). The following bleaching agent systems were used as reference substances:

- Sodium perborate tetrahydrate/TAED for the in situ preparation of peracetic acid according to a standard formulation with an average content of:

  20% by weight sodium perborate tetrahydrate and 4% by weight TAED in fully formulated heavy duty detergents;

  DPDDA (diperoxydodecanedioic acid) as an example of standard solid percarboxylic acid;

  stain removal salt based on sodium percarbonate or sodium perborate monohydrate and TAED.

The degree of bleaching in percent was determined as the wash result in the form of the average value obtained from 10 individual measurements, the determination being based on non-stained reference fabric being considered as 100% and stained unwashed fabric as being 0%. The degree of bleaching was determined by brightness measurements with a reflectance meter at a light wavelength of 456 nm against barium as standard. The following results were obtained.

a) Effectiveness of the compounds according to the invention in heavy duty detergents.

For the wash tests and results summarised in the following Table 2, the compounds according to the invention and the reference substances were incorporated into a phosphate-free base detergent powder without source of active oxygen commonly available on the market.

Table 2, Example 13 a)

No.	Bleaching agent		Conditions	Degree of bleaching in % in the case of fabrics			
	Type	relative quantity		Cotton		cotton/PE	
				Tea [1]	Red wine [2]	Tea [3]	Red wine [4]
A 1	PBS-4/TAED	0a equiv.	40 °C, washing machine	34	--		23
A 2	DPDDA	"	"	38	--		29
A 3	Acetylper-oxyborat	"	"	42	--	--	28
B 1	DPDDA	Weight - equivalent	60 °C, washing machine	25	22	13	8
B 2	Acetylper-oxyborate	"	"	47	34	36	22
C 1	-	-	60 °C, Linitest	22	12	--	--
C 2	PCS	Weight equivalent	"	27	18	--	--
C 3	PBS-4/TAED	"	"	27	18	--	--
C 4	Acetylper-oxyborate	"	"	52	32	--	--
C 5	Acetlyper-oxyborate	0a-equiv. to C2	"	39	24	--	--

A1, A2, B1, C1 to C3 = State of the art; A3, B2, C4 and C5 according to the invention

1) Test fabric WFK Tea 106

2) Test fabric EMPA Red wine 114

3) Test fabric cotton/polyester (50/50) with tea stained prepared in-house

4) Test Fabric cotton/polyester (50/50) with red wine stain prepared in-house

Table 2 Wash tests, Example 13a)

b) The effectiveness of the compounds according to the invention as a bleaching wash additive.

For the wash tests and results summarised in Table 3, the compounds according to the invention and the reference substances were incorporated into the following wash component:

W - fully formulated, commercial branded detergent (with bleaching component)

F - liquid detergent available on the market.

Example 14

The acetyl peroxyborate compounds according to the invention were examined for their disinfectant effect, particularly with regard to the microbicidal effectiveness (DLG suspension test). The period of activity was 2.5 minutes, the rate of destruction was determined as a function of the incubation temperature (20°C and 40°C) and of the pH. The test organisms used were Klebsiella aerogenes, Pseudomonas fluorescens, Staphylococcus aureus, Streptococcus faecalis.

The results summarised below were obtained. With a pH of 2.0, the acetyl peroxyborates according to the invention used in a concentration of 0.008% (80 mg/litre) safely destroyed the four bacteria tested at 20°C in the course of 2.5 minutes. It thus provides a better performance than the disinfectants commonly available on the market which contain approximately 8.4% PAA and approximately 17% by weight H_2O_2. At a pH of 5.6, the bacteria tested are safely destroyed with a concentration of 0.01% by weight. By increasing the temperature from 20°C to 40°C, a slight increase in the microbicidal effect can be achieved. In a further series of tests, Pseudomonas aeruginosa was used as test organism. This germ is safely destroyed at ambient temperatures with a concentration of 74 mg/litre. Furthermore, it was found that the acetylperoxyborates of the invention are not only effective against bacteria but also effective against fungi and viruses.

The results of the disinfection test provide proof of the fact that the acetyl peroxyborates according to the invention are excellent disinfectants particularly in the acid to neutral pH range. They are consequently suitable for disinfection in the hospital sector, for example, in the veterinary sector, in animal shed disinfection and in dairy hygiene, for example.

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Table 3, Effectiveness of the bleaching additive, Example 13 b)

No.	Bleaching agent			Conditions	Degree of bleaching % in the case of fabrics			
	Type	Relative quantity			Cotton		Cotton/BW	
					Tea [1]	Red wine [2]	Tea [3]	Red wine [4]
D 1	-	-	W	40 °C, washing machine	33	20	22	16
D 2	Stain removal salt/PCS	Oa-equivalent	"	"	33	23	24	16
D 3	Acetylperoxyborate	"	"	"	42	28	31	23
E 1	-	-	W	60 °C, Washing machine	44	35	27	16
E 2	Stain removal salts/PCS	Weight equivalent	"	"	50	41	37	24
E 3	DPDDA	"	"	"	49	40	32	21
E 4	Acetylperoxyborate	"	"	"	60	44	48	27
E 5	Acetylperoxyborate	40 % of the amount of Oa at E 2	"	"	57	39	39	23

Table 3 (continued)

F 1	-	-	F	40 °C Linitest	30	19	32	15
F 2	Stain removal salts/PCS	-	"	"	20	11	18	17
F 3	Acetylper-oxyborate	33 % of the amount of Oa at F 2	"	"	49	30	48	28
G 1	-	-	F	60 °C Linitest	22	18	--	--
G 2	Stain removal salts/PCS	Weight equivelent	"	"	8	9	--	--
G 3	Stain removal salts/PCS	"	"	"	16	13	--	--
G 4	Acetylper-oxyborate	Oa equivalent to G 2	"	"	34	26	--	--
G 5	Acetylper-oxyborate	Oa equivalent to G 3	"	"	26	19	--	--

D1, D2, E1 to E3, F1, F2, G1 to G3 = State of the art
D3, E4 and E5, F3, G4 and G5 = according to the invention

1) Test fabric WFK Tea 106
2) Test fabric EMPA Red wine 114
3) Test fabric cotton/polyester (50/50) with tea stained prepared in-house
4) Test Fabric cotton/polyester (50/50) with red wine stain prepared in-house

Example 15:

Feed materials: - Peracetic acid solution containing 21.4 % of PAA and 1 % of H_2O_2 prepared from

Acetic acid, 99 %	19 kg
Hydrogen peroxide, 85 %	3.4 kg
Acetic anhydride	3.2 kg
Sulphuric acid	0.22 kg
Turpinal SL	0.3 kg

- Borax (B=18.37 %) : 8.02 kg
- acetyl peroxyborate seeds : 2.0 kg
- Mg stearate : 0.15 kg

(all % data in % by weight)

a) Pre-formed peracetic acid

Hydrogen peroxide, to which sulphuric acid had been added, and acetic anhydride were metered simultaneously, but separately, into acetic acid at a rate such that a temperature of about 25°C was maintained. After adding Turpinal SL (1-hydroxyethane-1,1-diphosphonic acid) the mixture was heated at 35°C for a further 1 h. A peracetic acid solution having a low water content and the following typical composition was obtained: 21.4 % by weight of PAA, 1 % by weight of H_2O_2.

b) Boron raw material (= boron oxygen compound)

In order to prepare the boron raw material, borax pentahydrate was dried in a drier to an analytically determined boron content of about 18.4 % by weight.

c) Acetyl peroxyborate

The raw materials prepared under a) and b) of this example were combined, in a turbulent vacuum mixer which was equipped with rotary mixing blades (Fr >1), a rotary pinned-disc mill (Fr >>1) and a cooling/heating jacket, together with the acetyl peroxyborate obtained as undersize and oversize particles from sieving, and the mixture was reacted at 35°C to form a paste. The reaction time was about 50 min. Before the start of vacuum drying, magnesium stearate was added and excess acetic acid and water were removed at a product temperature of 35 to 55°C

(at about 60 to 70°C jacket heating) and under a vacuum of 50 to 100 mbar. The circumferential speed of the mixing blades was about 4 m/s (Fr about 9) during the reaction and drying. During this drying, the viscosity rose until the break-up stage was reached. During break-up, the circumferential speed of the mixing blades was reduced to about 1.5 m/s (Fr about 1.1). After passing through the break-up stage, that is to say at the start of disintegration of the composition, the pinned-disc mill was additionally switched on for 10 min (circumferential speed about 22 m/s, Fr about 700). During this period the particulate granules formed. Drying was then continued with the mixing blades at a circumferential speed of 4 m/s until the product was free-flowing.

19 kg of the granules from the above first drying step were sieved to obtain particle sizes of 0.4 to 5 mm and the fine and coarse fractions (3.1 kg) were recycled to the subsequent acetyl peroxyborate preparation.

The product granules sieved off in this way were fed to the second drying step for post-drying. For this purpose, the granules were dried in a fluidised bed by air drying at a fluidised bed temperature of about 60°C for 1 h. The loss on drying during this step was about 8 to 10 % by weight. About 14.3 kg of acetyl peroxyborate granules having the following composition and the following properties were obtained:

Sodium : 9.1 % by weight (acidimetric)
Boron : 9.6 % by weight (acidimetric)
Acetic acid : 23.6 % by weight (acidimetric)
Peracetic acid : 26.5 % by weight (iodometric)
H_2O_2 : 0.2 % by weight (cerometric)
Rate of dissolution: 97 % after 3 minutes (2 g/l, 20°C, 200 rpm)
Particle size analysis:
> 2.5 mm: 3.4 % by weight
> 1.0 mm: 39.4 % by weight
> 0.8 mm: 18.4 % by weight
> 0.63 mm: 19.9 % by weight
> 0.4 mm: 18.2 % by weight

> 0.4 mm: 0.7 % by weight

Bulk density: 0.8 kg/l

Stability determinations (typical values: % = % by weight):

- Avox loss at 110°C/15 h : 9 %
- Avox loss in closed vessel at 20°C/6 months: 1 %
- Avox loss in closed vessel at 40°C/4 weeks : 2-3 %

Microcaloric data at 40°C in closed glass ampoule:

- about 10 µW/g for the post-dried product
- about 400 µW/g for the pre-dried product

~~CLAIMS~~ THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A solid acetyl peroxyborate compound characterised by an active oxygen content of 2 to 8% by weight and by a content of peracetic acid, capable of being liberated on dissolution of the acetyl peroxyborate compound in water, of at least 10% by weight and a content of hydrogen peroxide of less than 4% by weight.

2. An acetyl peroxyborate compound according to claim 1, wherein the content of hydrogen peroxide which can be liberated on dissolution of the acetyl peroxyborate compound in water is less than 3% by weight.

3. An acetyl peroxyborate compound according to claim 2, wherein said content of hydrogen peroxide is less than 1.5% by weight.

4. An acetyl peroxyborate compound according to any preceding claim, wherein said content of peracetic acid is from 10% to 30% by weight.

5. An acetyl peroxyborate compound according to claim 4, wherein said content of peracetic acid is 20% to 30% by weight.

6. An acetyl peroxyborate compound according to any preceding claim and having characteristic IR bands in the region of approximately 1650 to 1670 cm^{-1} and in the region of approximately 1740 to 1755 cm^{-1}.

7. An acetyl peroxyborate compound according to any preceding claim and having a characteristic ^{13}C-NMR band (solid body spectroscopy) in the region of 18 to 19 ppm, measured against tetramethyl silane (TMS) as external standard.

8. An acetyl peroxyborate compound according to claim 7, wherein said ^{13}C-NMR band is at approximately 18.5 ppm.

9. An acetyl peroxyborate compound according to any preceding claim and having a differential calorimetry diagram which begins exothermically at approximately 135° to 140°C and continues exothermically with an exothermic peak in the region of approximately 170° to 185°C.

10. A washing, cleaning, bleaching agent and/or disinfectant composition containing an acetyl peroxyborate compound according to any preceding claim as

an active oxygen-generating component.

11. A solid bleaching agent and disinfectant composition according to claim 10.

12. A solid bleaching agent and disinfectant composition according to claim 11 in the form of powdered or granular material contained in a sachet or in the form of tablets fused into a film.

13. A process for the production of a solid acetyl peroxyborate compound according to claim 1, comprising:

a) reacting a solid boron oxygen compound with acetic acid and hydrogen peroxide, and/or

b) reacting a solid boron oxygen compound with a solution of peracetic acid in acetic acid, and/or

c) reacting a solid boron oxygen compound containing peroxygen with acetic acid,

if necessary with an addition of acetic anhydride and, according to process variants a) and b) if necessary with an addition of alkaline sodium salt, thereby to form a viscous solution, suspension or paste containing the acetyl peroxyborate; and then drying the acetyl peroxyborate thus formed.

14. A process according to claim 13, wherein the reaction is carried out at temperatures of up to 60°C.

15. A process according to claim 14, wherein the reaction is carried out at from 30° to 40°C.

16. A process according to any one of claims 13 to 15, wherein the reactants are used in process variants a) to c) in the following amounts:

a) in process variant a) the molar ratio of boron to the acetyl groups and to hydrogen peroxide is 1:(1 to 5): (0.2 to 2),

b) in process variant b) the molar ratio of boron to peracetic acid is 1:(0.2 to 2), preferably 1:(0.5 to 1), and

c) in process variant c) the molar ratio of peroxygen-containing boron oxygen compounds to the acetyl groups is 1:(1 to 10), preferably 1:(2 to 6).

17. A process according to any one of claims 13 to 16 wherein, according to process variant a), hydrogen peroxide with an H_2O_2 content of at least 70% by weight is used.

18. A process according to any one of claims 13 to 17 wherein, according to process variants a) and b), boron oxide and/or borax with a low or zero content of water of hydration is used as the boron oxygen compound.

19. A process according to any one of claims 13 to 16, wherein according to process variant c), sodium perborate with a low or zero content of water of hydration and with an Na:B ratio of 0.3:1 to 1:1 is used as the boron oxygen compound containing peroxygen.

20. A process according to claim 19, wherein sodium perborate mono hydrate and/or sodium perborate with an Na:B molar ratio of 0.4:1 to 0.7:1 is used as sodium perborate.

21. A process according to any of claims 13 to 20 including also the step of washing the acetyl peroxyborate product with a lower alcohol or an ester of a lower alcohol before drying the product or following an optional intermediate drying step but before the final drying.

22. A process according to claim 13, characterised in that, in accordance with process variant b), in a mixer which is provided with a rotary mixing tool and comminuting auxiliary mixing tool, with a heat exchange installation for cooling and heating and with a vacuum installation, at least the comminuting auxiliary mixing tool being characterised by a Froude number $Fr > 1$, preferably $Fr >> 1$,

b1) a pre-formed solution of peracetic acid in acetic acid and a boron oxygen compound having a low water content are reacted with one another in such a way that the temperature does not exceed about 40°C,

b2) seed crystals of acetyl peroxyborate are added, and

b3) a paste of the acetyl peroxyborate is formed by mixing at temperatures of up to about 45°C,

b4) a lubricant is optionally added to the paste and the paste is predried under vacuum at a product temperature of up to about 60°C, preferably of 35° to 55°C, until a granular acetyl peroxyborate forms, the

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comminuting auxiliary mixing tool being switched on for a brief period in the course of this pre-drying, after passing through a break-up stage and at the start of disintegration of the substantially pre-dried paste of acetyl peroxyborate, and subsequently, in step b5), either

b5.1) the pre-dried acetyl peroxyborate is completely post-dried under normal pressure and at a product temperature of up to about 80°C, preferably up to about 60°C, and the desired particle size fraction of the acetyl peroxyborate is then separated off by sieving, or

b5.2) the desired particle size fraction of the acetyl peroxyborate is first separated off from the coarse and/or fine fractions by sieving the pre-dried acetyl peroxyborate and then only that fraction having the desired particle size is completely post-dried under normal pressure at a product temperature of up to about 80°C, preferably up to about 60°C,

by which means the acetyl peroxyborate is obtained in the form of solid, particulate and flowable granules.

23. A process according to claim 22, wherein in step b1), borax hydrates of formula $Na_2B_4O_7.(H_2O)_{0-3}$ having a low water content, preferably borax hydrates containing about 1 to 2 molecules of water of hydration, are employed as boron oxygen compound.

24. A process according to claim 22 or claim 23, wherein the seed crystals in step b2) are added in an amount such as will be obtained as coarse and/or fine fractions on sieving in step b5.1) or b5.2), but at least in an amount of 2% by weight based on the reaction mixture in step b1).

25. A process according to any one of claims 22 to 24, wherein alkali metal salts and/or alkaline earth metal salts of relatively long-chain fatty acids, preferably magnesium stearate, are added as lubricant in step b4).

26. A process according to claim 25, wherein the lubricant is added in an amount of up to 5% by weight, preferably in an amount of up to 0.2 to 1% by weight, based on the reaction mixture in step b1).

DATED THIS 28th day of November, 1991

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ABSTRACT

New, stable, solid acetyl peroxyborate compounds are described which represent active oxygen-containing compounds based on acetic acid and boron oxygen compounds. The compounds according to the invention are characterised by their content of peracetic acid capable of being liberated instantly and directly in water, hydrogen peroxide being formed from these compounds only to a minor extent. The acetyl peroxyborates according to the invention are highly suitable for washing, bleaching and cleaning agent and disinfectant applications and as oxidising agents in organic synthesis.