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Kühling et al.

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[45] **Nov. 11, 1975**

[54] **COMPOSITION AND METHOD FOR ACTIVATING OXYGEN UTILIZING N-ACYLATED TETRAAZA-BICYCLO-NONANDIONES**

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Related U.S. Application Data

[62] Division of Ser. No. 235,032, March 15, 1972, Pat. No. 3,825,543.

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**[2].. **C11D 3/26**; C11D 7/32; C01B 15/00

[58] **Field of Search** 252/186, 103, 102, 99; 8/111

[56] **References Cited**

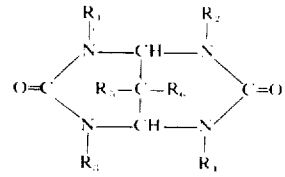
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[57] **ABSTRACT**

Solid oxidation compositions for bleaching and washing agents containing N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones of the formula



wherein at least two of R_1, R_2, R_3 and R_4 are acyls of organic carboxylic acids having 2 to 10 carbon atoms and the remainder of R_1, R_2, R_3 and R_4 are members selected from the group consisting of hydrogen and said acyl of organic carboxylic acids having 2 to 10 carbon atoms, and R_5 and R_6 are members selected from the group consisting of hydrogen and methyl, as well as the method of activation of percompounds in aqueous solutions at temperatures below 70°C utilizing said N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones.

15 Claims, No Drawings

COMPOSITION AND METHOD FOR ACTIVATING OXYGEN UTILIZING N-ACYLATED TETRAAZA-BICYCLO-NONANDIONES

REFERENCE TO A PRIOR APPLICATION

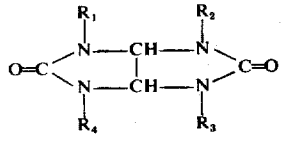
This application is a division of Ser. No. 235,032, filed Mar. 15, 1972, now U.S. Pat. No. 3,825,543.

THE PRIOR ART

Aqueous solutions of inorganic percompounds, particularly peroxide or perborates, have long since been used as oxidation and bleaching agents for the most varied types of materials. Of course, the active oxygen becomes effective with a sufficient speed for practical purposes only at temperatures in excess of 70°C, preferably in the range between 80°C and 100°C, so that these bleaching agents cannot be used with thermosensitive materials with which, taking into account the material to be bleached, work has to be carried out at relatively low temperatures.

It has already been proposed to add specific N-acyl compounds to the aqueous solutions of percompounds in order to activate the latter. According to German Published Application DAS No. 1,162,967, the compounds used for this purpose should contain at least two acyl groups attached to the same nitrogen atom, such as N,N,N'-triacetylmethylenediamine, N,N,N',N'-tetraacetylmethylenediamine and the like. According to German Published Application DAS No. 1,291,317, compounds of the general formula $RCO—NR_2—OCR_1$ serve this purpose, wherein R and R_1 signify C_{1-3} alkyl residues, while R_2 may constitute an optional organic radical which may be combined with R_1 to form a ring, if desired substituted, such as caprolactam, N-acylated barbitone, phthalimide, anthranil, N-acylated hydantoin or saccharine rings.

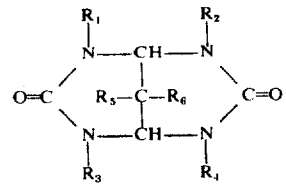
Copending U.S. patent application Ser. No. 141,372, filed May 7, 1971 now U.S. Pat. No. 3,715,184, describes the use of acylated glycolurils of the general formula



wherein at least two of the residues R_1 and R_4 constitute acyl residues having 2 to 8 carbon atoms, while the other residues signify hydrogen atoms and/or alkyl or aryl residues having 1 to 8 carbon atoms and/or acyl residues having 2 to 8 carbon atoms, as activators for percompounds. The acyl residues present in one molecule may be the same or different. Preferably, tetraacylglycolurils having similar C_{2-4} acyl residues are used, particularly tetraacetylglycoluril.

OBJECTS OF THE INVENTION

An object of the present invention is the obtaining of N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones of the formula



wherein at least two of R_1, R_2, R_3 and R_4 are acyls of organic carboxylic acids having 2 to 10 carbon atoms and the remainder of R_1, R_2, R_3 and R_4 are members selected from the group consisting of hydrogen and said acyl of organic carboxylic acids having 2 to 10 carbon atoms, and R_5 and R_6 are members selected from the group consisting of hydrogen and methyl.

Another object of the present invention is the development of a process for the production of the above N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones.

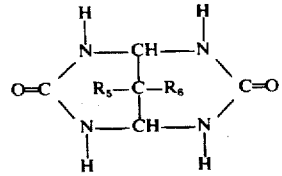
A yet further object of the present invention is the development of a method of activating aqueous solutions of percompounds at temperatures below 70°C by utilization of the above N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones.

A still further object of the present invention is the development of solid compositions for washing and bleaching agents containing the above N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones.

These and other objects of the invention will become more apparent as the description thereof proceeds.

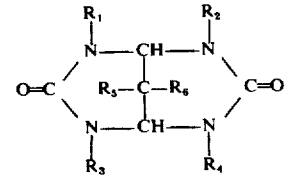
DESCRIPTION OF THE INVENTION

The present invention relates to new chemical substances which may be used as activators for percompounds which produce H_2O_2 in aqueous solution, said compounds being N-acylation products produced by acylating in a manner known per se a 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonane-3,7-dione of the general formula I:



I

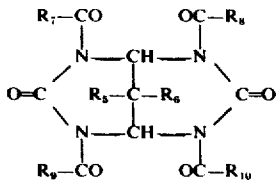
in which R_5 and R_6 individually signify a methyl residue or a hydrogen atom. The new acylation products preferably contain at least two acyl residues attached to the nitrogen atoms of the general formula II:



II

wherein at least two of R_1, R_2, R_3 and R_4 are acyls of organic carboxylic acids having 2 to 10 carbon atoms and the remainder of R_1, R_2, R_3 and R_4 are members selected from the group consisting of hydrogen and said acyl of organic carboxylic acids having 2 to 10 carbon atoms, and R_5 and R_6 are members selected from the group consisting of hydrogen and methyl.

When preferably four acyl residues are attached to the nitrogen atoms, the compounds correspond to the general formula III:



III

wherein R_7, R_8, R_9 and R_{10} represent hydrocarbon residues, optionally substituted having 1 to 9 carbon atoms, and R_5 and R_6 represent methyl residues or hydrogen atoms.

The acyls and acyls and hydrogen of R_1 to R_4 or the residues R_7 to R_{10} may be the same or different. Since compounds having similar acyls R_1 to R_4 or similar residues R_7 to R_{10} are simpler to produce, these compounds have greater practical importance. The acyls of R_1 to R_4 are preferably acyls of organic carboxylic acids having 2 to 10 carbon atoms selected from the group consisting of alkanoic acids having 2 to 4 carbon atoms, haloalkanoic acids having 2 to 4 carbon atoms, nitriloacetic acid, benzoic acid, alkylbenzoic acids having 8 to 10 carbon atoms, alkoxybenzoic acids having 8 to 10 carbon atoms, halobenzoic acids, nitrobenzoic acids, nitrilobenzoic acids, nitrotoluic acid, and halotoluic acid.

Among these acyls are acetyl, propionyl, butyryl, chloroacetyl, nitriloacetyl, benzoyl, toluoyl, p-methoxybenzoyl, m- or p-chlorobenzoyl, m- or p-nitrobenzoyl, nitrilobenzoyl, nitrotoluoyl and chlorotoluoyl. In formula III the group —CO—R_7 corresponds to R_1 of formula II where R_1 is acyl. If the residues R_7 to R_{10} are of aliphatic nature, they have preferably 1 to 3 carbon atoms. If aromatic residues are involved, they may contain up to 9 carbon atoms. Accordingly, the following are preferred as residues R_7 to R_{10}: methyl, ethyl, n- or i-propyl, phenyl, toluyl or xylyl residues. Suitable substituted groups are C_{1-3} alkoxyl groups, halogen atoms, nitro- or nitrile groups; m- or p-chloro-, or m- or p-nitro-substituted residues may be mentioned as examples of chloro- and/or nitro-substituted aromatic residues.

2,4,6,8-Tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione and its 9,9-dimethyl derivatives are of particular practical importance. However, the tetrapropionyl, tetrabutyryl or tetrabenzoyl derivatives may be used instead, as well as mixed acylated compounds such as acetyl-propionyl derivatives or acetyl-benzoyl derivatives.

Propylenedicarbamide serves as the raw material for producing these kinds of new compounds in which R_5 and R_6 represent hydrogen. The propylenedicarbamide is obtainable by condensation of urea with malonic dialdehyde or 1,1,3,3,-tetramethoxypropane [cf. Chemical Abstracts, Vol. 57 (1962), columns 13627 i/13628 (a) or Vol. 58 (1963), column 4552(c)]. Starting materials in which R_5 and R_6 represent methyl residues are obtained in accordance with the data given in German Published Application DAS No. 1,212,978.

In a manner known per se, these starting materials are converted into the acylation products by acylation, for example, with the corresponding carboxylic acids and anhydrides thereof, carboxylic acid halides, or with

ketenes. Sulfuric acid is suitable as the catalyst when acylating with carboxylic acid anhydrides. Advantageously, the process is carried out at a temperature of from 40° to 100°C. Mixed acylated products may be produced by converting the non-acylated starting material with a mixture of acylation agents; by acylation in stages using different acylating agents or by re-acylating a tetraacylated product with a different acylation agent.

The substances produced as technical raw products by this process are already usable in this state as activating agents for percompounds, but if importance is attached to their purity, they may be purified in a conventional manner by, for example, recrystallization or chromatographic processes.

Furthermore, the present invention relates to the use of the above-described N-acyl compounds as activators for H_2O_2 or percompounds producing H_2O_2 in water.

The percompounds to be activated in aqueous solution can be any type of inorganic or organic percompound which will release active oxygen in an aqueous solution. For economic reasons, the percompounds preferably utilized are inorganic peroxides, inorganic peracids, inorganic peroxyhydrates and products of the addition of hydrogen peroxide with inorganic and organic compounds.

Of the peroxides to be activated, hydrogen peroxide is of the greatest practical importance. It may be used as such, but may also be used in the form of its mostly solid peroxyhydrates or products of addition with inorganic and organic compounds. The latter include, for example, the products of addition of hydrogen peroxide to urea or melamine, and examples of the peroxyhydrates are the perborates, perortho-, perpyro-, and perpolyphosphates, percarbonates and persilicates. These peroxyhydrates are preferably soluble in water and are ordinarily utilized in the form of their alkali metal salts, such as their sodium salts. The activators, according to the invention, however, may also be used together with true peracids, such as for example, Caro's acid (peroxymonosulfuric acid, H_2SO_5) or peroxydisulfuric acid ($H_2S_2O_8$) or their salts.

Each acyl residue present in the acetylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione activator is able to activate an active oxygen atom of the percompound used. Therefore, in theory, the activator and percompound should be used in equivalent amounts for complete activation of the active oxygen present. In practice, however, satisfactory effects are attained in many cases even with substantially smaller amounts of activator, while on the other hand, the activator may also be used in relatively large excess.

It is possible to obtain perceptibly improved bleaching and oxidation values if only 1% of the total oxygen present is activated. An excess of activator is also possible. Generally, the quantity of activator to be used lies in the range of 5% to 500%, preferably from 10% to 200%, of the quantity required theoretically, 100% corresponding to an acyl residue per atom of active oxygen. If the tetraacetyl derivative is used as an activator, 2.38 parts by weight tetraacetyl derivative are theoretically required for a 100% activation for each part by weight of H_2O_2, and 0.51 parts by weight of the tetraacetyl derivative for one part by weight of $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$.

The activation, in accordance with the invention, of the oxygen is most clearly perceptible at temperatures in the range of 20°C to 70°C, especially from 30°C to

60°C. Nevertheless, it is possible to use higher temperatures up to 100°C for example, particularly when using deficient quantities of activator, so that chemically activated oxygen is used at temperatures up to 70°C, and thermally activated oxygen at higher temperatures, particularly temperatures in excess of 80°C. Depending upon the problem to be solved, it is possible for the technician, when using the activators according to the invention, either to reduce the temperature of treatment and/or to shorten the time of treatment, the temperature remaining the same. Finally, a low and a high temperature bleach can also be combined in one operation. In such cases it may be advantageous to add less than the theoretical amounts of activator; then at low temperatures only a part of the active oxygen present is activated, and the remainder is available for the bleaching at elevated temperatures.

The conditions to be maintained during operation with the activators according to the invention, such as for example, the concentration of the peroxide, temperature, pH value and time of treatment, depend substantially on the substance to be oxidized and/or bleached, and in some cases on the carrier material on or in which the substance to be bleached is present. The usually aqueous oxidizing or bleaching liquids may contain from 20 mg to 500 mg, preferably from 50 mg to 250 mg, per liter of active oxygen and have a pH value of from 4 to 12, preferably from 7 to 11.5, and particularly from 8 to 11. It should be kept in mind that the activators act by way of the intermediately formed percarboxylic acids. Therefore, carboxylic acid is produced during the oxidation or bleaching process and this should be neutralized by an alkali if a shift in the pH value is not desired.

As indicated, aqueous solutions of percompounds and the N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones, optionally with other ingredients as indicated below may be utilized. These aqueous solutions preferably contain sufficient percompounds to give a concentration of from 20 mg to 500 mg, preferably 50 mg to 250 mg per liter of active oxygen and sufficient N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione activator to provide from 0.05 to 5, preferably 0.1 to 2 acyls of the N-acylated activator per active oxygen atom.

The activators according to the invention may be used wherever percompounds, especially hydrogen peroxide or perborates, have previously been used as oxidizing and/or bleaching agents. This applies, for example, to the bleaching of oils, fats and waxes, to cosmetic skin and hair treatment, in disinfection or sterilization, in passivation of aluminum or other light metal surfaces, and especially in the bleaching of fibrous substances of all kinds.

The desired pH value is adjusted by addition of acid-, neutral- or alkaline-reacting substances, possibly by buffer mixtures, and particularly by additives which have also been co-employed in a corresponding, formerly customary treatment.

These frequently include the surface-active substances which serve to decrease the surface tension of the aqueous oxidizing or bleaching liquid, such as for example, soap or known synthetic detergents of anionic, non-ionic, amphoteric or cationic nature. When working in the alkaline range, alkaline substances may be added as well as inorganic or organic complex-forming compounds, especially complex-forming compounds suitable for binding the so-called hardness-producing substances in water or heavy metals which may possibly be present.

Furthermore, the invention relates to agents for producing aqueous oxidation baths effective in the cold, particularly alkaline bleaching and washing solutions, effective in the cold, for textiles. The composition of such agents lies generally in the range of the following recipe:

1% to 90% by weight of acylation products, serving as activators for percompounds, of N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones of formula II shown above,

99% to 10% by weight of other conventional constituents of aqueous oxidation liquids, particularly of alkaline bleaching or washing compositions for textiles.

The acylation products contain as activators in the products, in accordance with the invention, preferably at least two and particularly four acyl residues combined with nitrogen. The latter compounds correspond to formula III shown above.

In particular, the invention relates to solid oxidation compositions for bleaching and washing agents consisting essentially of from 5% to 90% by weight of an activator N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione, from 95% to 10% by weight of at least one alkaline-reacting builder salt, from 0 to 15% by weight of a surface-active compound selected from the group consisting of anionic surface-active compounds, non-ionic surface-active compounds and amphoteric surface-active compounds and from 0 to 30% by weight of other customary bleaching composition additions selected from the group consisting of percompound stabilizers, heavy metal complexing agents, corrosion inhibitors and optical brighteners, as well as solid, powdery-to-granular oxidation compositions for bleaching and washing agents consisting essentially of a water-soluble solid inorganic percompound in the form of its alkali metal salt and an activator N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione, said activator being present in an amount sufficient that from 0.05 to 5 acyls in said N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione are present per active oxygen atoms in said percompound.

The other conventional constituents of such agents of the above formulation include particularly those substances which are contained in bleaching, pre-washing or full washing agents, such as neutral- and/or alkaline-reacting builders, percompounds yielding H_2O_2 in aqueous solution, stabilizers for percompounds, complex formers, tensides or surface-active compounds, additives for increasing or reducing the foaming of the tensides, textile softeners, soil susupension agents, enzymes, optical brighteners, anti-corrosion agents, antimicrobial substances, perfumes, dyes, etc.

The activators may be coated or encased in any optional manner in such agents, so that the activators do not come into direct contact with the other constituents of the mixture. Thus the keeping qualities of such mixtures are considerably improved.

The products of the invention can be employed in the most varied technical fields anywhere it is important to activate oxygen in order to oxidize. It performs its oxidizing effect already at temperatures of 20°C to 70°C, preferably 30° to 60°C. Examples for such application fields are the cleaning of instruments, apparatus, pipe lines and vessels of wood, plastic, metal, ceramic, glass, etc., in the industry or in technical plants, the cleaning

of furniture, walls, the dishwashing in the household; and particularly the bleaching or laundering of textiles of any kind in industry, in commercial laundries and in the household. The low temperature bleaching with the use of chemically activated oxygen may also be combined with a high temperature bleaching in which the oxygen is activated thermally. There is, therefore, the possibility in the industry, in the commerce and in the household, dependent upon the problems to be solved, by the use of the activators of the invention either to lower the treatment temperature and/or to shorten the treatment at the same temperature, or, as already mentioned, to combine a low temperature and a high temperature bleaching.

In addition to cotton, regenerated cellulose or linen, it is possible in commerce or in the home to wash and-/or bleach the so-called "easy wash" textiles which are made from highly finished cotton or synthetic fibers, such as polyamide, polyester, polyacrylonitrile, polyurethane, polyvinylchloride or polyvinylidenechloride fibers, or which contain the latter mixed with other fibers. The textiles designated easy wash and sometimes as "non-iron" also include fabrics made from a mixture of synthetic fibers and cotton which may be specially finished.

Even if the activators to be used in accordance with the invention achieve their effect together with percompounds yielding H_2O_2 in aqueous solution, the agents in accordance with the invention do not necessarily have to contain percompounds. Agents containing activators, and containing no percompounds, may be of interest in the textile industry or in commercial laundries where percompounds are frequently added to the wash liquor in the form of hydrogen peroxide. Also such agents may also be of value in the home, if they are used in common with activator-free bleaching washing agents. For such purposes, it is advisable to put these agents on the market in the form of tablets or apportioned in packages.

In addition to the activators and the other additives, such products frequently contain certain quantities of auxiliary washing agents and washing agents of conventional, neutral and preferably alkaline-reacting builders, so that their composition is substantially in the range of the following formula:

5% to 90%, preferably 7% to 70%, by weight of activator in accordance with the invention,

95% to 10%, preferably 93% to 15%, by weight of neutral or preferably alkaline-reacting builders customary in auxiliary and washing agents,

0 to 15%, preferably 0 to 10%, by weight of tensides,

0 to 30%, preferably 0 to 10%, by weight of other conventional constituents of bleaching liquors, such as stabilizers for percompounds, complex formers for heavy metals, corrosion inhibitors, optical brighteners, etc.

With respect to their effects, the activators to be used in accordance with the invention are comparable to the best known products. Furthermore, they have the special advantage that all the acyl residues present are available for activating the oxygen. Thus, theoretically equivalent quantities of active oxygen and activator have to be used for completely activating the active oxygen present. In many cases in practice, it is sufficient to activate only a portion of the active oxygen. For example, it is possible to obtain perceptibly improved bleaching and oxidation values if only 1% of the total oxygen present is activated. A surplus of activator is also possible. In general, the quantity of the activator to be used is in the range from 5% to 500%, preferably from 10% to 200%, of the theoretically required quantity. 100% corresponds to one acyl residue for each atom of active oxygen. If the tetraacetyl derivative is used as an activator, 2.38 parts by weight of tetraacetyl derivative are required theoretically for 100% activation per part by weight of H_2O_2, and 0.51 parts by weight of tetraacetyl derivative are theoretically required for one part by weight of $NaBO_2.H_2O_2.3H_2O$.

Thus in products which contain percompounds yielding H_2O_2 in aqueous solution, as well as containing the activators in accordance with the invention, the quantitative proportion of active oxygen to activator should be in the above-mentioned range. The composition of such products is then substantially in the range of the following formula:

1. 5% to 100%, preferably 10% to 90%, by weight of a bleaching component comprising
   50% to 95% by weight of percompounds yielding H_2O_2 in aqueous solution
   50% to 5% by weight of activators in accordance with the invention, and
2. 95% to 0, preferably 90% to 10%, by weight of other conventional constituents of oxidation and bleaching agents, particularly of bleaching agents for textiles.

The activators in such products are preferably present in quantities such that the quantity of activator is from 5% to 500%, preferably 10% to 150%, of the theoretically required quantity, the theoretically required quantity (=100%) corresponding to one acyl residue for each active oxygen atom.

Such special products preferred for the textile industry or for commercial laundries contain preferably more than 40% by weight of percompounds and activators, while the bleaching, soaking, pre-washing and washing agents primarily used in the home generally contain no more than 40% by weight, preferably from 10% to 40%, particularly from 10% to 35% by weight of percompounds and activators.

The composition preferred for the textile industry, or for special products intended for commercial laundries, lies generally in the range of the following formula:

40% to 100%, preferably 45% to 80%, by weight of a bleaching component in accordance with the above definition,

60% to 0, preferably 55% to 20%, by weight of neutral or preferably alkaline-reacting builders,

0 to 40% by weight of tensides and, if required, additives for increasing or reducing the foaming of the tensides,

0 to 30%, preferably 1% to 20%, by weight of other conventional constituents of bleaching agents such as complex formers, textile softeners, soil suspension agents, enzymes, optical brighteners, anti-corrosion agents, anti-microbial substances, perfumes, dyes, etc.

The combination, in accordnce with the present invention, of activators and percompounds and, if required, stabilizers, anti-corrosion agents, and complex formers, may also be incorporated to advantage in the soaking agents to be used primarily in the home, usually at room temperature, particularly when the washing remains for a long period of time in the soaking bath. Such soaking agents have substantially the following composition:

0 to 5% by weight of tensides,

60% to 95% by weight, preferably 55% to 90% by weight, of preferably inorganic alkaline-reacting builders,

5% to 40%, preferably 10% to 40%, by weight of bleaching component in accordance with the above definition.

The composition of the prewashing, fine and full washing agents generally lies in the range of the following formula:

5% to 40% by weight of tensides,

5% to 80% by weight of neutral or preferably inorganic alkaline-reacting builders,

5% to 40% by weight, preferably 10% to 40%, by weight of bleaching component in accordance with the above definition,

0 to 20% by weight of other conventional constituents of such washing agents.

In such washing agents, the quantity of the neutral or preferably inorganic alkaline-reacting builder is usually at least equal to and preferably greater than the quantity of the tensides present.

The invention relates particularly to the use of the above-described activators in bleaching, soaking, prewashing, and main washing agents whose composition lies generally in the range of the following formula:

a. 2% to 40%, preferably 8% to 30%, by weight of tensides or combinations of tensides, comprising:
   0 to 100%, preferably 25% to 65%, by weight of anionic surface-active compounds of the sulfonate and/or sulfate type with preferably 8 to 18 carbon atoms in the hydrophobic residue,
   0 to 100%, preferably 5% to 40%, by weight of non-ionic surface-active compounds,
   0 to 100%, preferably 10% to 50%, by weight of soap,
   0 to 6%, preferably 0.5% to 3%, by weight of foam stabilizers,
   0 to 8%, preferably 0.5% to 5%, by weight of foam inhibitors.

b. 10% to 82%, preferably 35% to 75%, by weight of complex-forming and/or non-complex-forming builders, at least a portion of these builders having an alkaline reaction and the quantity of the alkaline-to-neutral reacting builders being preferably 0.5 to 7 times, and particularly 1 to 5 times, the total tenside combination.

c. 10% to 50%, preferably 10% to 45%, by weight of the combination, in accordance with the invention, of percompound, particularly perborate and activator and, if required, stabilizers for the percompounds, the quantity of this combination being preferably such that the content of active oxygen in the total washing agent amounts to 1% to 4%, preferably 1.5% to 3.5%, by weight.

d. 0 to 20%, preferably 2% to 15%, by weight of other washing agent constituents such as corrosion inhibitors, soil suspension agents, anti-microbial substances, optical brighteners, enzymes, perfumes, dyes, water.

Of particular practical importance are the washing agents which are intended for use in washing machines, preferably in drum-type washing machines in which the tenside component generally amounts to 7% to 30% by weight. This component generally has the following composition:

8% to 95%, preferably 25% to 75%, by weight of tensides (anionic surface-active compounds) of sulfonate and/or sulfate type with preferably 8 to 18 carbon atoms in the hydrophobic residue,

0 to 80%, preferably 10% to 50%, by weight of soap, insofar as when the soap is present, the quantitative proportion (sulfonate + sulfate): soap preferably lies in the range between 10:1 to 1:10, particularly 5:1 to 1:2,

0 to 35% by weight of non-ionic tensides,

0 to 6%, preferably 0.5% to 3%, by weight of foam stabilizers,

0 to 8%, preferably 0.5% to 5%, by weight of non-surface-active foam inhibitors, the foaming of the tenside component being reduced either by the simultaneous presence of tensides of the sulfonate and/or sulfate type and foam-inhibiting soap and/or by the presence of the non-surface-active inhibitors.

Sodium perborate tetrahydrate ($NaBO_2.H_2O_2.3H_2O$) has particular practical importance among the preferably inorganic percompounds yielding H_2O_2 in aqueous solution. Partially or completely dehydrated perborates, i.e., perborates dehydrated up to $NaBO_2.H_2O_2$, may be used instead of sodium perborate tetrahydrate. Alternatively, the borates $NaBO_2.H_2O_2$ (as described in German Pat. No. 901,287 or in U.S. Pat. No. 2,491,789) may be used in which the ratio Na_2O: B_2O_3 is less than 0.5:1 and preferably from 0.4 to 0.15:1, while the ratio H_2O_2 : Na is from 0.5 to 4:1. All these perborates may be replaced entirely or partially by other inorganic percompounds, particularly by peroxyhydrates, for example, the peroxyhydrates of the ortho-, pyro- or polyphosphates, particularly of tripolyphosphates, and of the carbonates. These peroxyhydrates are preferably soluble in water and are ordinarily utilized in the form of their alkali metal salts, such as the sodium salts.

It is advisable to incorporate quantities of from 0.25% to 10% by weight of conventional water-soluble and/or water-insoluble stabilizers for stabilizing the percompounds in the products of the invention. The magnesium silicates of a ratio of $MgO:SiO_2 = 4:1$ to 1:4, preferably 2:1 to 1:2, and particularly 1:1, generally obtained by precipitation from aqueous solutions, are suitable as water-insoluble stabilizers for percompounds. These compounds, for example, amount to from 1% to 8%, preferably 2% to 7%, of the weight of the entire preparation. Other alkaline earth metal silicates, cadmium silicates or tin silicates of corresponding composition may be used instead of the magnesium silicates. Water-containing oxides of tin are also suitable as stabilizers. Stabilizers soluble in water, which may be present together with stabilizers insoluble in water, are the organic complex formers whose quantity can amount to 0.25% to 5% preferably 0.5% to 2.5% of the weight of the entire preparation.

The tensides contain in the molecule at least one hydrophobic residue of mostly 8 to 26, preferably 10 to 22 and especially 10 to 18 carbon atoms, and least one anionic, nonionic or amphoteric water-solubilizing group. The preferably saturated hydrophobic residue is mostly aliphatic, but possibly also alicyclic in nature. It may be combined directly with the water-solubilizing groups or through intermediate members, such as through benzene rings, carboxylic-acid ester links, carbonamide links or sulfonic-acid amide links as well as through ether- or ester-like residues of polyhydric alcohols.

Soaps, which are derived from natural or synthetic fatty acids, possibly also from resin acids or naphthenic

acids, are utilizable as anionic detergent substances, especially if these acids have iodine values of not more than 30 and preferably less than 10.

Among the synthetic anionic tensides, the sulfonates and sulfates possess particularly practical importance.

The sulfonates include, for example, alkylbenzenesulfonates with preferably straight-chain C_{9-15}, especially C_{10-14} alkyl residues, alkanesulfonates, obtainable from preferably saturated aliphatic C_{8-18}, especially C_{12-18} hydrocarbons by sulfochlorination or sulfoxidation, mixtures of alkenesulfonates, hydroxyalkanesulfonates and alkanedisulfonates, known under the name of "olefinsulfonates", which are formed by acidic or alkaline hydrolysis of the sulfonation products which first result from terminal or non-terminal C_{8-18} and preferably C_{12-18} olefins by sulfonation with sulfur trioxide. The sulfonates, utilizable according to the invention, include also salts, preferably alkali metal salts of α-sulfo fatty acids and salts of esters of these acids with mono or polyhydric alcohols with 1 to 4, and preferably 1 to 2 carbon atoms.

Further useful sulfonates are salts of fatty acid esters of hydroxyethanesulfonic acid or of dihydroxypropanesulfonic acid, the salts of the fatty alcohol esters of lower aliphatic or aromatic sulfomono- or dicarboxylic acids, containing 1 to 8 carbon atoms, the alkylglycerylether sulfonates and the salts of the amide-like condensation products of fatty acids or sulfonic acids with aminoethanesulfonic acid.

Tensides of the sulfate type include fatty alcohol sulfates, especially those derived from coconut fatty alcohols, tallow fatty alcohols or from oleyl alcohol, also sulfatized fatty acid alkylamides or fatty acid monoglycerides and sulfated alkoxylation products of alkylphenols (C_{8-15} alkyl), fatty alcohols, fatty acid amides, or fatty acid alkylolamides with 0.5 to 20, preferably 1 to 8, and particularly 2 to 4 ethylene and/or propyleneglycol residues in the molecule.

As anionic tensides of the carboxylate type, for example, the fatty acid esters or fatty alcohol ethers of hydroxycarboxylic acids, are suitable as well as the amide-like condensation products of fatty acids or sulfonic acids with aminocarboxylic acids, such as glycocoll, sarcosine or with protein hydrolysates.

The anionic tensides are mostly present as salts of the alkali metals, particularly of sodium, as well as the ammonium salts and salts of lower alkylamines or lower alkylolamines.

The nonionic tensides, for the sake of simplicity called hereafter "Nonionics", include the polyethyleneglycol ethers, obtained by addition of from 4 to 100, preferably 6 to 40 and especially 8 to 20 mols of ethylene oxide to fatty alcohols, alkylphenols, fatty acids, fatty amines, fatty acid amides or sulfonic acid amides, as well as the still water-soluble adducts of propylene oxide or butylene oxide to the above. Furthermore, products known by the trade name "Pluronics" or "Tetronics" belong to the Nonionics. These products are obtained from water-insoluble polypropyleneglycols or from water-insoluble propoxylated lower aliphatic alcohols with 1 to 8, preferably 3 to 6 carbon atoms, or from water-insoluble propoxylated lower alkylenediamines, by ethoxylation until water-soluble. Finally, the partly water-soluble reaction products of the above-named aliphatic alcohols with propylene oxide, known as "Ucon-Fluid" can also be used as Nonionics.

Further useful Nonionics are fatty acid alkylolamides or sulfonic acid alkylolamides, derived, for example, from mono- or diethanolamine, from dihydroxypropyl amine or other polyhydroxyalkyl amines, such as the glycamines. Also the oxides of higher tertiary amines with a hydrophobic alkyl residue and two shorter alkyl and/or alkylol residues, with up to 4 carbon atoms each, can be considered as Nonionics.

Amphoteric tensides contain in the molecule both acidic groups, such as carboxyl, sulfonic acid, sulfuric acid half esters, phosphonic acid and phosphoric acid partial ester groups, and also basic groups, such as primary, secondary, tertiary and quaternary ammonium groups. Amphoteric compounds with quaternary ammonium groups belong to the type of the betaines. Carboxy, sulfate and sulfonate betaines have a particularly practical interest because of their good compatibility with other tensides.

The foaming power of the tenside can be increased or reduced by combination of suitable tenside types, as well as changed by additions of non-tenside organic substances.

Suitable foam stabilizers, particularly in tensides of the sulfonate or sulfate type, are surface-active carboxy or sulfobetaines, as well as the above-named non-ionics of the alkylolamide type. Moreover, fatty alcohols or higher terminal diols have been suggested for this purpose.

A reduced foaming power, that is desirable for the use in washing machines, is often attained by combination of different tenside types, such as of sulfates and/or sulfonates and/or of nonionics, on the one hand, with soaps, on the other hand. In soaps, the foam inhibition increases with the degree of saturation and the number of carbons in the fatty acid residue. Soaps derived from saturated C_{20-24} fatty acids have been proven good as foam inhibitors.

The non-tenside foam inhibitors included N-alkylated aminotriazines, optionally containing chlorine, which are obtained by the reaction of 1 mol of cyanuric acid chloride with 2 to 3 mols of a mono- and/or dialkylamine with 6 to 20, preferably 8 to 18 carbon atoms in the alkyl radicals. similarly effective are propoxylated and/or butoxylated aminotriazines, such as, products that are obtained by the addition of from 5 to 10 mols of propylene oxide to 1 mol of melamine and further addition of from 10 to 50 mols of butylene oxide to this propylene-oxide derivative.

Other non-tenside foam inhibitors are water-insoluble organic compounds, such as paraffins or halogenated paraffins with melting points below 100°C, aliphatic C_{18} to C_{40} ketones as well as aliphatic carboxylic acid esters which contain in the acid or alcohol residue, optionally also in both of these residues, at least 18 carbon atoms (such as triglyceride or fatty acid/fatty alcohol esters). These compounds can be used for the inhibition of foam, above all in combinations of tensides of the sulfate and/or sulfonate type with soaps.

As particularly low-foaming nonionics which can be used both alone, particularly in the agents for automatic dishwashing, and also in combination with anionic, amphoteric and nonionic tensides and to reduce the foaming power of better foaming tensides, addition products of propylene oxide to the above-described surface active polyethyleneglycol ethers are suitable as well as the also above-described "Pluronic", "Tetronic" and "Ucon-Fluid" types.

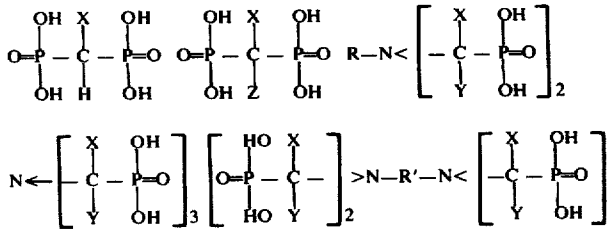
All weakly acidic, neutral and alkaline reacting organic or organic salts, particularly inorganic or organic sequestering agents, are suitable as builders.

Weakly acidic, neutral or alkaline reacting salts usable according to the invention are, for example, the bicarbonates, carbonates, borates or silicates of the alkali metals, also mono-, di- or trialkali metal orthophosphates, di- or tetraalkali metal pyrophosphates, alkali metal metaphosphates known as sequestering agents, alkali metal sulfates as well as the alkali metal salts of organic non-surface-active sulfonic acids, carboxylic acids and sulfocarboxylic acids, containing from 1 to 8 carbon atoms. To them belong, for instance, the water-soluble salts of benzene-, toluene- or xylene-sulfonic acid, water-soluble salts of sulfoacetic acid, sulfobenzoic acid or salts of sulfodicarboxylic acids as well as the salts of the acetic acid, lactic acid, citric acid and tartaric acid.

Further usable as builders are the water-soluble salts, such as the alkali metal salts, of higher-molecular weight polycarboxylic acids, particularly polymerizates of maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, methylenemalonic acid and citraconic acid. Also mixed polymerizates of these acids with each other, or with other polymerizable substances, such as, ethylene, propylene, acrylic acid, methyacrylic acid, crotonic acid, 3-butenecarboxylic acid, 3-methyl-3-butenecarboxylic acid as well as with vinylmethyl ether, vinyl acetate, isobutylene, acrylamide and styrene, are usable.

Also suitable as sequestering builders are the weakly acidic reacting metaphosphates and the alkaline reacting polyphosphates, particularly tripolyphosphate. These compounds may be replaced completely or partially by organic sequestering agents.

The organic sequestering agents include, for example, nitrilotriacetic acid, ethylenediaminetetraacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid, polyalkylenepolyamine-N-polycarboxylic acids and other known organic sequestering agents. Also combinations of different sequestering agents may be used. The other known sequestering agents include also di- and polyphosphonic acids of the following constitutions:



wherein R represents alkyl and R′ represents alkylene residues with 1 to 8, preferably 1 to 4 carbon atoms; X and Y represent hydrogen atoms or alkyl radicals with 1 to 4 carbon atoms and Z represents the groups —OH, —NH_2 or —NXR. For a practical use, the following compounds are considered above all: methylenediphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, aminotri-(methylenephosphonic acid), methylamino- or ethylamino-di-(methylenephosphonic acid), and ethylenediaminetetra-(methylenephosphonic acid). All these sequestering agents may be present as free acids, or preferably as their alkali metal salts.

Soil-suspending agents which keep the dirt loosened from the fiber suspended in the liquor, and thus prevent the graying, can also be utilized in the washing agents and washing auxiliaries. For this, water-soluble colloids, mostly organic in nature, are suitable, such as the water-soluble salts of polymeric carboxylic acids, glue, gelatins, salts of ethercarboxylic acids or ethersulfonic acids of starch or cellulose or salts of acidic sulfuric acid esters of cellulose or starch. Also water-soluble polyamides, containing acidic groups, are suitable for this purpose. Furthermore, soluble starch preparations and starch products other than the above-named, such as degraded starch, aldehyde starches, etc. may be used. Also polyvinylpyrrolidone is usable.

The ingredients of the washing agents and washing auxiliaries, particularly the builders are mostly so selected, that the preparations react neutral to distinctly alkaline in aqueous solution. Preferably, the pH-value of a 1% solution of the preparation mostly lies in the range from 7 to 12. Fine-washing agents have mostly a neutral to weakly alkaline reaction (pH-value = 7 to 9.5), while soaking, pre-washing and boiling-washing agents are more strongly alkaline (pH value from 9.5 to 11.5, preferably from 10 to 11.5). The action of the activators is associated with alkali consumption. Thus, the builders present should prevent the pH value from dropping below the stated minimum values during the entire treatment period.

The enzyme preparations to be used are mostly a mixture of enzymes with different effects, such as proteases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerases, lyases, transferases, desmolases or nucleases. Of particular interest are the enzymes, obtained from bacteria strains or from fungi, such as Bacillus subtilis or Streptomyces griseus, particularly proteases and amylases, which are relatively stable towards alkalis, percompounds, and anionic tensides and are still effective at temperature up to 70°C.

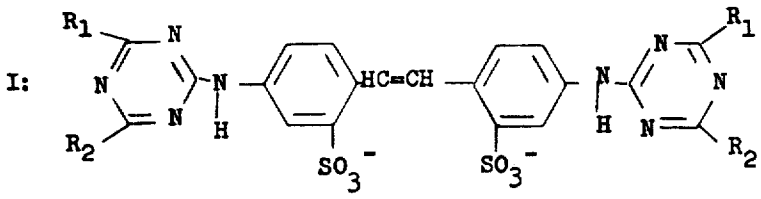
Enzyme preparations are marketed by the manufacturers mostly as aqueous solutions of the active substances or as powders, granulates or as cold-sprayed products. They frequently contain sodium sulfate, sodium chloride, alkali metal ortho-, pyro- and polyphosphates, particularly tripolyphosphate, as fillers. Dust-free preparations are particularly valued. These are obtained in a known manner by incorporating of oily or pasty Nonionics or by granulation with the aid of melts of water-of-crystallization-containing salts in their own water-of-crystallization.

Enzymes may be incorporated which are specific for certain types of soil, for example, proteases or amylases or lipases. Preferably, combinatons of enzymes with different effects are used, particularly combinations of proteases and amylases.

The optical brighteners which can be utilized in the compositions are mostly, if not exclusively, derivatives of aminostilbenesulfonic acid, or of diaminostilbenedi-

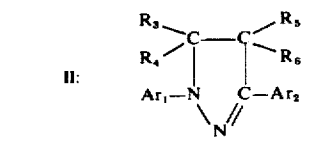
sulfonic acid, of diarylpyrazolines, of carbostyril, of 1,2-di-(2-benzoxazolyl)-ethylene or 1,2-di-(2-benzimidazolyl)-ethylene, of benzoxazolyl-thiophene and of the coumarins.

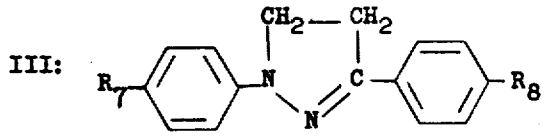
Examples of brighteners from the class of the diaminostilbenedisulfonic acid derivatives are compounds, according to formula I:



In the formula, R_1 and R_2 represent alkoxy, amino, or residues of aliphatic, aromatic or heterocyclic, primary or secondary amines as well as residues of aminosulfonic acids, where the aliphatic residues present in the above groups, contain preferably 1 to 4 and particularly 2 to 4 carbon atoms, while the heterocyclic ring systems are mostly 5 to 6 membered rings. As aromatic amines the residues of the aniline, of the anthranilic acid or the anilinesulfonic acid are preferred. Brighteners, derived from the diaminostilbenedisulfonic acid, are mostly used as cotton brighteners. The following products, derived from formula I, are commercially available, where R_1 represents the residue $-NHC_6H_5$ and R_2 may represent the following residues: $-NH_2$, $-NHCH_3$, $-NHCH_2CH_2OH$, $-NHCH_2CH_2OCH_3$, $-NHCH_2CH_2CH_2OCH_3$, $-N(CH_3)CH_2CH_2OH$, $-N(CH_2CH_2OH)_2$, morpholino-, $-NHC_6H_5$, $-NHC_6H_4SO_3H$, $-OCH_3$. Some of these brighteners are, in regard to their fiber affinity, regarded as transitional types to the polyamide brighteners, such as the brightener with $R_2 = -NHC_6H_5$. The compound 4,4'-bis-(4-phenyl-1,2,3-triazole-2-yl)-2,2'-stilbenedisulfonic acid belongs also to the cotton brighteners of the diaminostilbenedisulfonic acid type.

The polyamide brighteners, some of which have a certain affinity for wool fibers, include diarylpyrazolines of the formulae II and III:





In the formula II R_3 and R_5 represent hydrogen, alkyl and aryl, optionally substituted by carboxyl, carbonamide or carboxylic acid ester groups, R_4 and R_6 represent hydrogen or lower alkyl, Ar_1 and Ar_2 represent aryl radicals, such as phenyl, diphenyl or naphthyl, which may carry further substituents, such as hydroxy, alkoxy, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, carboxylic acid esters, sulfonic acid, sulfonamide and sulfone groups or halogen atoms. Commercially available brighteners of this type are derived from the formula III, where the radical R_7 may represent the groups Cl, $-SO_2NH_2$, $-SO_2CH=CH_2$, and $-COOCH_2CH_2OCH_3$, while R_8 mostly represents a chlorine atom. Also the 9-cyanoanthracene belongs to the polyamide brighteners.

The polyamide brighteners further include aliphatically or aromatically substituted aminocoumarins, such as 4-methyl-7-dimethylamino-coumarin or 4-methyl-7-diethylaminocoumarin. Further usable as polyamide brighteners are the compounds 1-(2-benzimidazolyl)-2-(1-hydroxyethyl-2-benzimidazolyl)-ethylene and 1-ethyl-3-phenyl-7-diethylamino-carbostyril. Suitable as brighteners for polyester and polyamide fibers are the compounds 2,5-di-(2-benzoxazolyl)-thiophene and 1,2-di-(5-methyl-2-benzoxazolyl)-ethylene.

If the brighteners together with other ingredients of the invention products are present as aqueous solution or paste, and are to be transformed to solids by heat drying, it is recommended to incorporate organic sequestering agents in amounts of at least 0.1%, preferably 0.2% to 1% by weight of the solid products in order to stabilize the brighteners.

The present invention will be further described with reference to the following specific examples which are, however, not to be deemed limitative in any respect.

EXAMPLES

The Examples designated H describe the manufacture of the products produced in accordance with the invention; the Examples designated V describe the use of said products, and the Examples designated A and B describe compositions containing the activators of the invention.

The propylenedicarbamide used as the raw material was produced by treating urea with 1,1,3,3-tetramethoxypropane in accordance with Kageyama et al, Chemical Abstracts, 57, (1962), column 13627(i) or in accordance with Kobayashi, Chemical Abstracts, 58, (1963), column 4552(c). The propylenedicarbamide so produced had a melting point of 310° to 311°C. According to the data in the literature, the melting point is 310°C. A molecular weight of 156.15 is calculated from the empirical formula $C_5H_8N_4O_2$. A molecular mass m/e = 156 was determined by mass spectography. The analysis data found are compared with the calculated values below:

Calculated: C, 38.46%; H, 5.16%; N, 35.88%. Found: C, 38.51%; H, 5.15%; N, 36.18%.

The 9,9-dimethyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione also used as the raw material was produced in accordance with the data in German Published Application DAS No. 1,212,978 by condensation of urea with α-chloroisobutyl-methylether in the presence of dimethylformamide and $SOCl_2$ or $COCl_2$. The melting point of the product was in excess of 360°C. A molecular weight of 184.20 was calculated

from the empirical formula $C_7H_{12}N_4O_7$. A molecular mass m/e = 184 was determined by mass spectography. The analysis data, calculated and found, were as follows:

Calculated: C, 44.65%; H, 6.62%; N, 30.44%. Found: C, 45.04%; H, 6.26%; N, 30.64%.

The IR, NMR and mass spectra of the products of the process of Examples 1, 5 and 8 to 11, the IR spectra of the products of the process of Examples 2, 3 and 4, and the IR and mass spectra of the products of the process of Example 7 were obtained. In all cases, the spectra obtained corresponded to the anticipated spectra. The molecular masses found by mass spectography, and the elementary analysis of the process products, are given in the individual examples. For further identification of the tetraacetyl compounds obtained in accordance with Examples 2, 3 and 4, the melting points of mixtures of these substances were checked with the tetraacetyl compound obtained in accordance with Example 1. The melting point was not lowered in any instance.

EXAMPLE H 1

The production of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione by reaction of propylenedicarbamide with acetic acid anhydride.

1 ml of 70% perchloric acid was added to a suspension of 8.1 gm (0.052 mol) of propylenedicarbamide in 55 gm (0.54 mol) of acetic acid anhydride at room temperature. The temperature increased to 35°C. While heating to 50°C, stirring was carried out for 7.5 hours and the solution obtained was then filtered off from the nonconverted starting material (0.8 gm of propylenedicarbamide). The tetraacylated propylenedicarbamide, which separated from the clear filtrate after adding isopropanol, had a melting point of 181° to 183°C after recrystallization from isopropanol. The yield amounted to 5.4 gm, corresponding to 35.7% of theory relative to propylenedicarbamide converted.

A molecular weight of 324.3 was calculated from the empirical formula $C_{13}H_{16}N_4O_6$ (m/e = 324). The calculated analysis data corresponded to the analysis data found:

Calculated: C, 48.15%; H, 4.97%; N, 17.28%. Found: C, 47.89; H, 4.94; N, 17.59.

EXAMPLE H 2

The production of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione by reaction of propylenedicarbamide with acetic acid anhydride.

15.6 gm (0.1 mol) of propylenedicarbamide was slowly added to a solution of 4 ml of 100% sulfuric acid in 110 ml of acetic acid anhydride over a period of 2.5 hours at 55° to 60°C. The mixture was stirred for 10 hours at 55° to 60°C and the undissolved portions were filtered off. Isopropanol was added, under cooling, to the residue obtained after reduction in volume of the filtrate. 18.5 gm (56.5% of theory) of the tetraacetyl derivative having a melting point of 174.5° to 177.5°C was precipitated after scratching on the vessel wall.

EXAMPLE H 3

The production of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione by reaction of propylenedicarbamide with acetylchloride.

After adding 2 ml of 100% sulfuric acid to a mixture of 15.6 gm (0.1 mol) of propylenedicarbamide and 78.5 gm (1 mol) of acetylchloride, the mixture was stirred for 34 hours while refluxing. The residue, obtained after filtering off the undissolved portions and distilling off the excess acetylchloride in vacuo, was dissolved in chloroform and washed three times with water until a neutral reaction was obtained.

After drying the chloroform solution over anhydrous Na_2SO_3 and evaporating the chloroform in vacuo, 17.2 gm (65.7% of theory) crude product was obtained. The yield amounted to 10.5 gm (40.2% of theory) after recrystallization from ethanol. The recrystallized product had a melting point of 178° to 182°C.

EXAMPLE H 4

The production of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione by reaction of propylenedicarbamide with ketene.

Ketene was introduced for 8 hours into a suspension of 15.6 gm (0.1 mol) of propylenedicarbamide in 60 gm of glacial acetic acid and 1 ml of 100% sulfuric acid. The mixture was allowed to cool and the non-converted propylenedicarbamide (about half the amount used) was filtered off. By adsorptive filtration on a column of silica gel (0.05–0.2 mm; eluting mixture, benzene/chloroform = 95:5), 2.3 gm of raw product having a melting point of 170° to 182°C was obtained from the viscous oil obtained after vaporizing the filtrate. The melting point rose to 181.5° to 183.5°C upon recrystallizing once from isopropanol.

EXAMPLE H 5

The production of 2,4,6,8-tetrapropionyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione by reaction of propylenedicarbamide with propionic acid anhydride.

A suspension of 15.6 gm (0.1 mol) of propylenedicarbamide in 150 ml of propionic acid anhydride and 4 ml of 100% sulfuric acid was stirred for 9 hours at 60°C. The slightly cloudy solution was filtered after standing overnight and subsequently concentrated in vacuo. The raw product was isolated from this solution in the same manner as described in Examples H1 and H 2 for the tetraacetyl derivative. 18.4 gm (48% of theory) of raw product, having a melting point of 142° to 144.5°C was obtained. The melting point of the pure product obtained upon recrystallization was 144.5° to 146°C.

A molecular weight of 380.4 is calculated from the empirical formula $C_{17}H_{24}N_4O_6$ (m/e = 380); the calculated analysis data corresponded to the analysis data found:

Calculated: C, 53.68%; H, 6.36%; N, 14.73%. Found: C, 53.56; H, 6.63; N, 14.74.

EXAMPLE H 6

The production of mixed tetraacylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones by reaction of diacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione with propionic acid anhydride.

A suspension of 48.0 gm (0.2 mol) of diacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione (manufactured in accordance with Example H 8) in 78.0 gm (0.6 mol) of propionic acid anhydride and 6 ml of 100% sulfuric acid was stirred at 98° to 100°C, until a clear solution had formed after 6 hours. The residue obtained after evaporation was dissolved in chloroform and extracted three times with water. After drying the chloroform solution with anhydrous Na_2SO_4 and evaporating, a light yellow oil was produced which crystallized after adding isopropanol, cooling and scratching the glass wall. After vacuum filtering the iso-

propanol and washing the residue with isopropanol and methanol, there remained 10 gm of a substance mixture which had a melting point of 135° to 141°C and which, according to the mass spectrum, constituted a mixture of tetrapropionyl-, monoacetyl-tripropionyl- and diacetyl-dipropionyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-diones (m/e = 380 or 366 or 352).

According to a thin layer chromatogram, the reaction mixture contained the said three compounds in substantially the same proportions. The empirical formula $C_{16}H_{22}N_4O_6$ and an average molecular weight of 366.38, is calculated therefrom. The calculated analysis data corresponded to the analysis data found:

Calculated: C, 52.45%; H, 6.05%; N, 15.29%. Found: C, 52.49%; H, 6.01%; N, 15.59%.

EXAMPLE H 7

The production of diacetyl-dibutyryl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione by reaction of dibutyryl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione with acetic acid anhydride.

A suspension of 17.8 gm (0.06 mol) of dibutyryl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione, obtained in accordance with Example H 9, in 18.4 gm (0.18 mol) of acetic acid anhydride and 1.5 ml of 100% sulfuric acid was stirred for 4 hours at 50° to 60°C. The acylation product was isolated as described in Example H 6. 5.2 gm (22.8% of theory) of the raw product was obtained having a melting point of 103° to 107°C. The melting point was 113° to 116°C after recrystallization twice from methanol or ethanol.

A molecular weight of 380.4 (m/e = 380) is calculated from the empirical formula $C_{17}H_{24}N_4O_6$. The calculated analysis data corresponded to the analysis data found:

Calculated: C, 53.68%; H, 6.36%; N, 14.73%. Found: C, 52.34%; H, 6.07%; N, 15.08%.

EXAMPLES H 8 to H 10

The production of N,N'-diacylated-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione.

Suspensions of 0.1 to 0.2 mol of propylenedicarbamide in 0.3 to 0.6 mol of the corresponding carboxylic acid anhydride were heated in the presence of 100% sulfuric acid, cooled to 5° to 10°C after the reaction was completed, and methanol or acetonitrile was added. The precipitated diacyl derivatives were vacuum filtered and recrystallized. The working conditions used in each case and the characteristic values of the process products are given below.

EXAMPLE H 8

The production of N,N'-diacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione.

Starting mixture:
15.6 gm (0.1 mol) propylenedicarbamide
30.6 gm (0.3 mol) acetic acid anhydride,
3 ml H_2SO_4
Reaction conditions: 2.5 hours, 60°C
Raw yield: 11.3 gm (47.2% of theory)
Melting point after recrystallization from water: 249°C to 251°C
Values: Empirical formula $C_9H_{12}N_4O_4$
Molecular weight: 240.2 (m/e = 240)
Analysis: Calculated: C, 45.00%; H, 5.05%; N, 23.32%. Found: C, 45.04; H, 5.00; N, 23.83.

EXAMPLE H 9

The production of N,N'-dipropionyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione.

Starting mixture:
31.2 gm (0.2 mol) propylenedicarbamide
78.0 gm (0.6 mol) propionic acid anhydride, 8 ml H_2SO_4
Reaction conditions: 7 hours, 70°C
Raw yield: 17.5 gm (32.7% of theory)
Melting point after recrystallization from acetonitrile: 239° to 241°C.
Values: Empirical formula $C_{11}H_{16}N_4O_4$
Molecular weight: 268.3 (m/e = 268)
Analysis: Calculated: C, 49.25%; H, 6.01%; N, 20.88%. Found: C, 49.23; H, 5.92; N, 21.03.

EXAMPLE H 10

The production of N,N'-dibutyryl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione.

Starting mixture:
15.6 gm (0.1 mol) propylenedicarbamide
47.4 gm (0.3 mol) butyric acid anhydride,
2.5 ml H_2SO_4
Reaction conditions: 4 hours, 60° to 70°C
Raw yield: 9.0 gm (30.4% of theory)
Melting point after recrystallization from acetonitrile: 216° to 219°C
Values: Empirical formula $C_{13}H_{20}N_4O_4$
Molecular weight: 296.3 (m/e = 296)
Analysis: Calculated: C, 52.69%; H, 6.80%; N, 18.91%. Found: C, 52.61; H, 6.75; N, 19.63.

EXAMPLE H 11

The production of 2,4,6,8-tetraacetyl-9,9dimethyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione by reaction of dimethylpropylenedicarbamide with acetic acid anhydride.

A suspension of 21 gm (0.114 mol) of dimethyl-propylenedicarbamide in 116 gm (1.14 mol) of acetic acid anhydride and 3.5 ml of 100% sulfuric acid was stirred for 5 hours at 95° to 100°C. After evaporating the clear dark reaction solution in vacuo, a residue was obtained which was purified by dissolution in isopropanol, cooling and vacuum filtering, and recrystallizing from approximately 400 ml isopropanol. The yield then amounted to 18.0 gm (25% of theory). The melting point of the product was 164° to 174°C. This product was purified by column chromotography through silica gel (eluent: benzene:chloroform = 60:40) and recrystallizing from isopropanol. The melting point was then 180° to 183°C.

A molecular weight of 352.35 is calculated from the empirical formula $C_{15}H_{20}N_4O_6$ (m/e = 352). The calculated analysis data corresponded to the analysis data found:

Calculated: C, 51.13%; H, 5.72%; N, 15.90%. Found: C, 51.08; H, 5.75; N, 15.84%.

EXAMPLES H 12 to H 17

The production of the tetrabenzoyl derivatives, chloro- or nitro-substituted, if required, of 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione or of 9,9-dimethyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione.

The substances produced are given in the following tables. They were produced in accordance with the following general specification.

0.15 to 0.3 mol of benzoylchloride, substituted if required, were added drop by drop at room temperature to an agitated suspension of 0.05 mol of the substance to be benzoylated in 100 ml of dry pyridine. The starting substances went into solution during 3 hours heating of this reaction mixture to 115° to 120°C. The liquid was filtered off, insofar as the reaction product separated, as in the case of p-nitrobenzoylchloride, for example. However, if the reaction product remained in solution, the pyridine was distilled in vacuo and the product of the process was isolated from the dried residue by mixing with water. Heavily colored impurities could be removed by washing with chloroform.

The following tables contain details concerning the process conditions, the yields, the solvents used for recrystallization and the melting points. The raw yields relate to the tetrabenzoyl derivatives.

EXAMPLES H 12 to H 14

Tetrabenzoyl Derivatives of 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Example No.	Benzoylating Agent	Raw Yield	Melting Point After Recrystallization from
12	0.2 mol benzoylchloride	15.2 gm, 55% of theory	234° to 236.5°C/ benzene
13	0.15 mol p-chlorobenzoylchloride	11.0 gm, 41% of theory	243° to 245.5°C/ acetone/dimethylformamide
14	0.3 mol p-nitrobenzoylchloride	18.0 gm, 48% of theory	247° t0 249°C/ dimethylformamide

EXAMPLES H 15 to H 17

Tetrabenzoyl Derivatives of 9,9-dimethyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Example No.	Benzoylating Agent	Raw Yield	Melting Point After Recrystallization from
15	0.3 mol benzoylchloride	29.5 gm, 98% of theory	255° to 257°C/ acetone
16	0.3 mol p-chlorobenzoylchloride	32.0 gm, 87% of theory	254° to 258.5°C/ chloroform
17	0.3 mol p-nitrobenzoylchloride	17.0 gm, 44% of theory	267° to 270°C/ dimethylformamide

The usability of the activators to be used in accordance with the invention was demonstrated in the following examples by the following general experimental procedures.

Aqueous solutions, containing 0.615 gm of $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$ (4 mMol) and 2.5 gm of $Na_4P_2O_7 \cdot 10\ H_2O$ per liter, after addition of either 1, 2 or 4 mMol of activator (corresponding to 0.25, 0.5 and 1 mol of activator per mol of active oxygen) were heated to 24°, 45° and 60°C, respectively. The solutions were agitated and maintained at the stated temperatures during the entire experiment. 100 ml of the solution were drawn off by means of a pipette at specific intervals of time, immediately added to a mixture of 250 gm of ice and 15 ml of glacial acid and then, after addition of about 0.35 gm of potassium iodide, were titrated with 0.1 N sodium thiosulfate solution using starch as an indicator.

Under the stated experimental conditions, about 8 ml of thiosulfate solution were consumed with a 100% activation of the peroxy compound used. The thiosulfate consumed and the percentage amount of the activated peroxy compound are given in the tables. The "blank value" characterizes the consumption of thiosulfate of the test solutions before adding the activator and thus the maximum quantity of the activated oxygen.

EXAMPLE V 1 a

Activation of 1 mol of perborate with 0.25 mol of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C: ml 0.1N $Na_2S_2O_3$	% 0 Activated	at 45°C: ml 0.1N $Na_2S_2O_3$	% 0 Activated	at 60°C: ml 0.1N $Na_2S_2O_3$	% 0 Activated
1	2.44	30.3	3.71	45.8	4.81	59.3
5	4.18	51.9	5.62	69.4	5.72	70.5
10	5.08	63.1	5.98	73.8	5.38	66.3
15	5.51	68.4	6.11	75.4	4.79	59.1
30	5.82	72.3	5.86	72.3	3.30	40.7
60	6.37	79.1	5.25	64.8	1.46	18.0
Blank Value	8.05	100.0	8.10	100.0	8.11	100.0

EXAMPLE V 1 b

Activation of 1 mol of perborate with 0.5 mol of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml. 0.1N $Na_2S_2O_3$	% O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	% O Activated
1	6.00	74.0	7.49	93.6	7.82	96.5
5	7.86	97.0	7.82	97.8	7.24	89.4
10	8.00	98.8	7.72	96.5	6.74	83.2
15	8.00	98.8	7.61	95.1	6.00	74.1
30	8.10	100.0	7.22	90.2	4.34	53.6
60	8.02	99.0	6.53	81.6	1.70	22.0
Blank Value	8.10	100.0	8.00	100.0	8.10	100.0

EXAMPLE V 1 c

Activation of 1 mol of perborate with 1 mol of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	% O Activated
1			7.00	85.9	7.56	92.8
5			7.58	93.0	7.42	91.0
10			7.84	96.2	6.78	83.2
15			7.82	95.9	6.24	76.6
30			7.44	91.2	4.90	60.0
60			6.90	84.6	3.00	36.8
Blank Value			8.15	100.0	8.15	100.0

EXAMPLE V 2 a

Activation of 1 mol of perborate with 0.5 mol of 2,4,6,8-tetrapropionyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	% O Activated
1	0.46	5.8	0.87	10.6	1.28	15.8
5	1.18	14.9	2.57	31.4	3.93	48.5
10	2.19	27.6	3.94	48.2	5.22	64.4
15	2.86	36.0	4.82	48.9	5.42	66.9
30	4.89	61.6	6.02	73.6	4.62	57.0
60	6.81	85.8	5.75	70.3	2.51	31.0
Blank Value	7.84	100.0	8.18	100.0	8.10	100.0

EXAMPLE V 2 b

Activation of 1 mol of perborate with 1 mol of 2,4,6,8-tetrapropionyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	% O Activated
1	0.26	3.3	1.21	14.8	2.22	27.2
5	1.17	14.8	4.27	52.3	5.20	63.7
10	2.67	33.8	6.44	78.8	5.83	71.4
15	4.00	50.6	6.93	84.7	5.65	69.2
30	7.31	92.5	6.73	82.4	4.76	38.3
60	6.87	86.9	6.38	78.1	3.08	37.5
Blank Value	7.90	100.0	8.17	100.0	8.16	100.0

EXAMPLE V 3 a

Activation of 1 mol of perborate with 0.25 mol of the mixed acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione according to Example H 6

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	at 24°C % O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	at 45°C % O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	at 60°C % O Activated
1	0.35	4.3	1.42	17.5	2.95	36.5
5	1.61	19.9	3.65	45.1	4.62	57.2
10	2.76	34.0	4.45	54.9	4.75	58.8
15	3.63	44.8	4.88	60.2	4.65	57.5
30	4.99	61.5	5.35	66.0	3.55	43.9
60	5.98	63.7	5.25	64.8	1.59	19.0
Blank Value	8.11	100.0	8.10	100.0	8.08	100.0

EXAMPLE V 3 b

Activation of 1 mol of perborate with 0.5 mol of the mixed acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione according to Example H 6

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	at 24°C % O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	at 45°C % O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	at 60°C % O Activated
1	0.54	6.7	3.02	37.4	4.10	50.7
5	2.70	33.4	6.36	78.7	7.06	87.4
10	5.36	66.2	7.18	88.9	7.14	88.4
15	6.59	81.5	7.30	90.3	6.97	86.3
30	7.76	95.9	7.47	92.5	5.82	72.0
60	7.75	95.8	7.17	88.7	3.82	47.3
Blank Value	8.09	100.0	8.08	100.0	8.08	100.0

EXAMPLE V 3 c

Activation of 1 mol of perborate with 1 mol of the mixed acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione according to Example H 6

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	at 24°C % O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	at 45°C % O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	at 60°C % O Activated
1	0.78	9.75	4.18	51.8	6.15	76.0
5	4.08	50.5	7.32	90.7	7.41	91.6
10	7.26	89.4	7.23	89.6	7.10	87.8
15	6.93	85.8	7.32	90.7	6.85	84.7
30	6.16	76.2	7.18	89.0	5.90	72.9
60	6.13	75.9	6.70	83.0	4.55	56.2
Blank Value	8.08	100.0	8.07	100.0	8.09	100.0

EXAMPLE V 4 a

Activation of 1 mol of perborate with 0.5 mol of N,N-diacetyl-2,4,6,8-tetraaza-bicyclo(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	at 24°C % O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	at 45°C % O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	at 60°C % O Activated
1	1.46	18.1	3.23	39.8	4.34	54.0
5	3.25	40.3	4.84	59.7	5.37	66.8
10	4.01	49.8	5.44	67.1	5.21	64.8
15	4.43	55.0	5.68	70.0	4.79	59.6
30	5.08	63.2	5.75	70.9	3.44	42.8
60	5.52	68.5	5.23	64.9	1.67	20.8
Blank Value	8.06	100.0	8.11	100.0	8.04	100.0

EXAMPLE V 4 b

Activation of 1 mol of perborate with 1 mol of N,N'-diacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	% O Activated
1	2.23	27.7	4.86	59.3	6.21	77.6
5	4.36	54.2	6.69	81.6	7.09	88.5
10	5.41	67.2	7.13	86.9	6.80	85.0
15	5.93	73.7	7.30	89.0	6.40	80.0
30	6.55	81.4	7.12	86.8	5.23	75.4
60	6.20	77.0	6.78	82.7	3.10	38.7
Blank Value	8.05	100.0	8.20	100.0	8.00	100.0

EXAMPLE V 5 a

Activation of 1 mol of perborate with 0.5 mol of 2,4,6,8-tetraacetyl-9,9-dimethyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	% O Activated
1	1.08	13.5	4.48	55.9	7.14	89.0
5	5.20	64.8	7.15	89.2	7.13	88.9
10	7.29	90.9	7.28	90.8	6.75	84.2
15	7.65	95.4	7.29	90.9	6.44	80.3
30	7.72	96.3	7.03	87.7	5.40	67.3
60	7.90	98.5	6.34	79.1	3.54	44.1
Blank Value	8.02	100.0	8.02	100.0	8.02	100.0

EXAMPLE V 5 b

Activation of 1 mol of perborate with 1 mol of 2,4,6,8-tetraacetyl-9,9-dimethyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione

Sampling After x Minutes	Activation obtained at 24°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 45°C ml 0.1N $Na_2S_2O_3$	% O Activated	at 60°C ml 0.1N $Na_2S_2O_3$	% O Activated
1	7.10	88.8	7.10	87.9	6.95	86.0
5	5.62	70.3	7.42	91.8	7.05	87.3
10	5.60	70.0	7.66	94.8	6.58	81.4
15	5.98	74.8	7.50	92.8	6.20	76.7
30	6.98	87.3	7.33	90.7	7.14	63.6
60	7.48	93.5	6.88	85.1	3.70	46.8
Blank Value	8.00	100.0	8.08	100.0	8.08	100.0

It is preferred that solutions of H_2O_2, or of compounds yielding H_2O_2, having a concentration of from 10 to 200 gm H_2O_2 per liter are used for oxidative treatment of hair and, advantageously, the solutions have a pH value of from 7 to 11, preferably from 8 to 10.5. The pH value may be adjusted by adding buffer substances. Mixtures of ammonium salts of strong acids and aqueous ammonia have proved to be successful. The amount of activator to be used corresponds to the above data.

EXAMPLE V 6

For the purpose of bleaching hair, dyeing hair by means of oxidation dyes, and oxidative after-treatment of hair after setting under the effect of reducing thio compounds, an aqueous solution produced in the following manner is used, for example:

6 gm of $(NH_4)_2SO_4$, 15 ml of a 25% aqueous NH_3 and 37 ml of a 30% H_2O_2 solution are dissolved in 30 ml of water, and made up to 100 ml with water.

If such a solution is used to make dark-blonde hair lighter, the hair is made perceptibly lighter within 30 to 90 minutes at 20° to 30°C. However, if 40 gm of 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicylco-(3,3,1)-nonan-3,7-dione or its 9,9-dimethyl derivative is added, the hair is made considerably lighter within the same time. Alternatively, however, the treatment time can be shortened.

If the equivalent amount of 2,4,6,8-tetrapropionyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione or its 9,9-dimethyl derivative is used, the bleaching activation is less at the beginning. Thus it is an easier matter to make the color only partially lighter up to a specific desired tint.

The following examples describe compounds of some of the preparations in accordance with the invention. The salt-like constituents, salt-like tensides, other organic salts and inorganic salts are present as sodium salts unless otherwise expressly stated. The designations and abbreviations used are as follows:

"ABS" signifies the salt of an alkylbenzenesulfonic acid, having from 10 to 15, preferably from 11 to 13, carbon atoms in the alkyl chain, obtained by condensing straight chain olefins with benzene and sulfonating the alkylbenzene thus obtained.

"Alkanesulfonate" signifies a sulfonate obtained from paraffins having from 12 to 16 carbon atoms by way of sulfoxidation.

"HPK-sulfonate" or "HT-sulfonate" signifies the α-sulfonates obtained from the methyl esters of a hardened palm kernel or a hardened stearic fatty acid by sulfonating with SO_3.

"Olefinsulfonate" signifies a sulfonate which is obtained from olefin mixtures having from 12 to 18 carbon atoms by sulfonating with SO_3 and hydrolyzing the sulfonation product with aqueous sodium hydroxide. The olefinsulfonate consists substantially of alkenesulfonate and hydroxyalkanesulfonate, but also contains small amounts of disulfonates. Products may also be used which are manufactured from α-position or non-terminal olefins.

"CA-sulfate" and "TA-sulfate" signify the salts of sulfated, substantially saturated fatty alcohols produced by reduction of coconut fatty acid or tallow fatty acid.

"CA-EO-sulfate" signifies the sulfated products of addition of 2 mols of ethyleneoxide to 1 mol of coconut fatty alcohol.

"OA + 10 EO", "CA + 20 EO" and "Fs-amide + 8 EO" signify the products of addition of ethyleneoxide (EO) to industrial oleyl alcohol (OA) or coconut alcohol (CA) or coconut fatty acid amide, the number characterizing the molar amount of ethyleneoxide added to 1 mol of the initial compound.

"CA + 9 EO + 12 PO" signifies a non-ionic obtained by converting 1 mol of "CA + 9 EO" with 12 mols of propyleneoxide.

"Carboxybetaine" and "sulfobetaine" signify the obtained by reacting 1 mol of coconut alkyldimethylamine with 1 mol of chloroacetic acid or 1 mol of propane sultone.

"CMC" signifies the salt of carboxymethyl cellulose.

"NTA", "EDTA", "DETPA", "HEDP" and "ATMP" signify the salts of the nitrilotriacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, hydroxyethanediphosphonic acid and aminotrimethylenephosphonic acid.

"Perborate" (mono) and "perborate" (tetra) signifiy a perboratemono- and perboratetetrahydrate of the approximate compositions $NaBO_2.H_2O_2$ and $NaBO_2.H_2O_2.3\ H_2O$.

"Activator" signifies 2,4,6,8-tetraacetyl-2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione.

The composition of the fatty acid mixtures from which the soaps B, C and D were produced is given in the following table. The table also includes the composition of the fatty acid mixtures of a soap G. If the soaps B, C and D given in the examples are replaced by the same quantity of soap G, the foaming capacity of this washing agent will be significantly greater than the corresponding washing agent having soap C, although it will be somewhat less than the corresponding washing agent having the soap B.

Composition of the Fatty Acid Mixtures Corresponding to the Soaps

No. of Carbon Atoms Present in the Fatty Acid	% By Weight of the Fatty Acid Constituent in the Soap			
	B	C	D	G
C_{10}	2	2	4	1
C_{12}	19	21	16	6
C_{14}	8	6	10	5
C_{16}	4	16	25	28
C_{18}	22	33	45	60
C_{20}	8	4	—	—
C_{22}	37	18	—	—
Iodine number of the fatty acid mixture	4	8	6	4

A mixture of about 45% of a di-(alkylamino)-monochlorotriazine and about 55% of a N,N',N''-trialkylmelamine was used as a foam inhibitor. In all these triazine derivatives, the alkyl residues were present as a mixture of homologs with from 8 to 18 carbon atoms. Monochlorotriazine derivatives or trialkylmelamine could be used with a similar result. In the described products which contained synthetic sulfates or sulfonates together with soap, the other non-tenside-like foam inhibitors mentioned in the specification could be used, such as paraffin oil or paraffin. During the manufacture of the agents or preparations, the foam inhibitor used was dissolved in a suitable organic solvent or was sprayed in the melted state onto the moving pulverulent preparation by means of a nozzle.

The following Examples A1 to A7 and B1 to B10 described the composition of some of the preparations in accordance with the invention which may be used as special products in the textile industry, in commercial laundries, and, even if to a smaller extent, in the home. The products in accordance with Examples A1 to A7 do not contain percompounds. They can be used together with percompounds or bleaching, washing or auxiliary washing agents containing percompounds. On the other hand, the preparations according to Examples B1 to B10 themselves contain percompounds.

Constituent of the Preparation	% By Weight of the Constituent in the Preparation According to Example						
	A1	A2	A3	A4	A5	A6	A7
Activator	31	31	27	60	45	19	38
Tenside	2					8	5
$Na_2O{\cdot}SiO_2$	21	20	19	33	25	12	24
$Na_4P_2O_7$	46		54			32	6
Na_2CO_3		49		7	30	29	27

Any of the substances mentioned in the specification can be used as tensides, preferably one of the anionic or non-ionic substances mentioned under the examples. If these preparations are also to have the ability to absorb heavy metal ions, 0.2 to 5% by weight of EDTA, DETPA or ATMP are added to them with a corresponding reduction in the content of the $Na_4P_2O_7$ and/or Na_2CO_3.

Constituent of the Preparation	% By Weight of the Constituent in the Preparation According to Example									
	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
Perborate (mono)	—	—	41.0	22.6	38.1	—	34.8	38.0	47.1	32.2
Perborate (tetra)	41.0	36.1	—	—	—	43.5	—	—	—	—
Activator	23.0	19.7	21.3	23.5	16.5	23.3	27.3	22.8	10.1	24.8
Tenside	—	2.0	—	5.0	—	—	1.0	—	—	—
$Na_2O \cdot SiO_2$	16.0	19.6	13.5	15.2	24.0	14.9	17.4	15.0	30.0	20.0
EDTA	2.0	—	1.0	0.2	—	—	—	0.7	—	—
DETPA	—	—	—	—	—	—	0.5	—	—	—
ATMP	—	1.6	—	—	—	—	—	—	—	—
$Na_4P_2O_7$	—	23.1	—	—	21.4	—	—	—	12.8	4.5
Na_2CO_3	18.0	—	23.2	33.5	—	18.3	19.0	23.5	—	18.5

The composition of some of the washing agents in accordance with the invention may be seen from Examples W1 to W10.

Constituent of the Preparation	% By Weight of the Constituent in the Preparation According to Example				
	W1	W2	W3	W4	W5
ABS	6.9	—	4.9	6.0	—
HPK-sulfonate	—	1.6	1.2	—	4.0
Olefinsulfonate	—	1.8	—	1.5	—
Soap B	4.1	—	3.1	—	1.0
Soap D	—	—	—	4.2	—
OA + 10 EO	2.5	1.2	1.9	—	—
CA + 20 EO	—	—	—	—	7.0
CA + 9 EO + 12 PO	—	2.0	—	—	6.6
Fs-amide + 8 EO	—	—	—	3.5	—
Foam inhibitor	—	0.6	—	0.2	—
$Na_5P_3O_{10}$	35.0	36.5	38.5	30.1	—
$Na_2O \cdot 3.3\ SiO_2$	5.4	1.5	5.4	2.9	4.5
Na_2SO_4	0.3	0.5	3.4	3.6	5.0
NTA	—	—	—	—	15.0
EDTA	0.7	—	1.2	0.1	—
HEDP	—	—	—	—	14.0
ATMP	—	1.1	—	—	—
CMC	0.6	1.0	0.3	0.5	1.5
$MgSiO_3$	1.4	2.4	2.2	1.0	1.0
Perborate (mono)	—	—	17.4	16.3	16.0
Perborate (tetra)	2.14	25.0	—	—	—
Activator	11.8	13.7	9.0	17.0	7.0
Na_2CO_3	8.2	9.4	5.7	11.0	5.0
Brightener	0.50	0.25	0.25	0.35	0.36
Residual Water					

Constituent of the Preparation	% By Weight of the Constituent in the Preparation According to Example				
	W6	W7	W8	W9	W10
ABS	—	6.0	5.0	—	—
Alkanesulfonate	2.9	—	—	5.0	—
HT-sulfonate	—	—	—	5.0	8.5
CA-sulfate	—	1.5	1.2	—	—
TA-sulfate	—	0.5	0.3	—	—
CA-EO-sulfate	—	—	1.5	5.0	—
Soap C	7.6	—	—	2.0	7.5
OA + 10 EO	5.0	—	—	—	2.7
CA + 9 EO + 12 PO	1.8	—	—	—	—
Carboxybetaine	—	—	0.5	—	—
Sulfobetaine	—	0.7	—	0.6	—
Foam Inhibitor	—	0.5	0.5	0.6	0.6
$Na_5P_3O_{10}$	35.5	40.0	36.4	41.1	38.0
$Na_2O \cdot 3.3\ SiO_2$	5.5	5.5	4.0	4.5	—
Na_2SO_4	0.55	1.0	2.5	—	0.8
CMC	—	2.0	1.3	1.7	1.2
NTA	—	—	15.0	—	—
EDTA	—	—	0.2	—	—
DETPA	—	0.2	—	—	—
HEDP	—	6.0	7.0	9.0	—
ATMP	—	—	—	—	1.5
$MgSiO_3$	2.3	2.5	2.0	—	—
Perborate (mono)	—	14.0	10.0	14.0	15.6
Perborate (tetra)	19.0	—	—	—	—
Activator	10.2	11.0	6.0	3.0	12.0
Na_2CO_3	6.5	7.0	4.0	2.0	8.0
Brightener	0.25	0.40	0.35	0.25	0.29

-continued

Constituent of the Preparation	% By Weight of the Constituent in the Preparation According to Example				
	W6	W7	W8	W9	W10
Residual Water					

The bleaching liquors, particularly washing liquors manufactured by using the agents in accordance with the invention exhibit a better bleaching effect than obtained with known activators, both at treatment temperatures of, for example, 30° to 45°C and at higher temperatures up to boiling. The higher degree of whiteness of the wash is perceptible particularly when optical brighteners are simultaneously present.

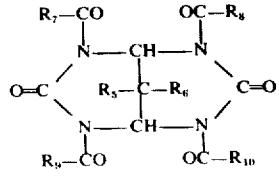
In principle, these statements also apply to working at lower temperatures of, for example, 10° to 25°C. although a correspondingly longer treatment period is necessary in this lower range of temperature.

Similar results are obtained if the tetraacetyl derivative serving as activator in the preparations in accordance with the invention is replaced by the tetrapropionyl or tetrabenzoyl compounds or the mixed acylated derivatives, for example, acetyl and propionyl residues or acetyl and benzoyl residues. This also applies to the 9,9-dimethyl derivatives. Similar results are also obtained if the perborates contained in the examples are replaced by other compounds, such as percarbonates, yielding H_2O_2 in aqueous solution.

The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients disclosed herein or known to those skilled in the art, may be employed without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. The method of activating aqueous solutions of per-compounds selected from the group consisting of hydrogen peroxide and water-soluble in organic peroxyhydrates containing from 20 mg to 500 mg per liter of active oxygen, said solution having a pH of 4 to 12 and a temperature of from 10°C to 70°C which consists essentially of adding to said aqueous solution in activator N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione of the formula



wherein each of the R_7CO, R_8CO, R_9CO and $R_{10}CO$ are the same acyl of organic carboxylic acids selected from the group consisting of alkanoic acids having 2 to 4 carbon atoms, haloalkanoic acids having 2 to 4 carbon atoms, benzoic acid, alkylbenzoic acids having 8 to 10 carbon atoms, halobenzoic acids, nitrobenzoic acids, nitrotoluic acids, and halotoluic acids, R_5 and R_6 are members selected from the group consisting of two hydrogens and two methyls, said activator being added to said aqueous solution in an amount sufficient that from 0.05 to 5 acyls in said N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione are present per active oxygen atom in said aqueous solution.

2. The method of claim **1**, wherein said aqueous solution has a pH of from 7 to 11.5.

3. The method of claim **2**, wherein said aqueous solution has a pH of from 8 to 11.

4. The method of claim **1**, wherein said activator is added to said aqueous solution in an amount sufficient that from 0.1 to 2 acyls in said N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione are present per active oxygen atom in said aqueous solution.

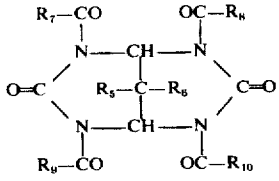
5. The method of claim **1**, wherein from 50 mg to 250 mg per liter of active oxygen are present in said aqueous solution.

6. The method of claim **1**, wherein said percompound is hydrogen peroxide and is present in said aqueous solution in an amount of from 10 to 200 gm per liter, said aqueous solution being utilized in the oxidative treatment of human hair.

7. The method of claim **6**, wherein said aqueous solution has a pH of from 7 to 11.

8. The method of claim **7**, wherein said aqueous solution has a pH of from 8 to 10.5.

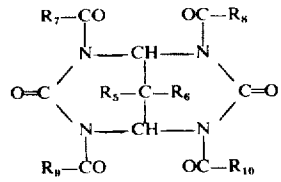
9. Solid oxidation compositions for bleaching and washing agents consisting essentially of from 5% to 90% by weight of an activator N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione of the formula



wherein each of the R_7CO, R_8CO, R_9CO and $R_{10}CO$ are the same acyl of organic carboxylic acids selected from the group consisting of alkanoic acids having 2 to 4 carbon atoms, haloalkanoic acids having 2 to 4 carbon atoms, benzoic acid, alkylbenzoic acids having 8 to 10 carbon atoms, halobenzoic acids, nitrobenzoic acids, nitrotoluic acids, and halotoluic acids, and R_5 and R_6 are members selected from the group consisting of two hydrogens and two methyls, from 95% to 10% by weight of at least one alkaline-reacting builder salt, from 0 to 15% by weight of a surface-active compound selected from the group consisting of anionic surface-active compounds, non-ionic surface-active compounds and amphoteric surface-active compounds, and from 0 to 10% by weight of percompound stabilizers.

10. The solid oxidation compositions for bleaching and washing agents of claim **9** containing from 7% to 70% by weight of said activator, from 15% to 93% by weight of said builder salt and from 0% to 10% by weight of said surface-active compound.

11. Solid powdery to granular oxidation compositions for bleaching and washing agents consisting essentially of a water-soluble solid inorganic percompound in the form of its alkali metal salt and an activator N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione of the formula



wherein each of the R_7CO, R_8CO, R_9CO and $R_{10}CO$ are the same acyl of organic carboxylic acids selected from the group consisting of alkanoic acids having 2 to 4 carbon atoms, haloalkanoic acids having 2 to 4 carbon atoms, benzoic acid, alkylbenzoic acids having 8 to 10 carbon atoms, halobenzoic acids, nitrobenzoic acids, nitrotoluic acids, and halotoluic acids, and R_5 and R_6 are members selected from the group consisting of two hydrogens and two methyls, said activator being present in an amount sufficient that from 0.05 to 5 acyls in said N-acylated 2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonan-3,7-dione are present per active oxygen atoms in said percompound.

12. The solid, powdery to granular oxidation compositions for bleaching and washing agents of claim **11**, wherein from 0.1 to 2 acyls are present per active oxygen atoms in said percompound.

13. The solid, powdery to granular oxidation compositions for bleaching and washing agents of claim **11**, wherein up to 10% by weight of a stabilizer for percompounds is present.

14. The solid, powdery to granular oxidation compositions for bleaching and washing agents of claim **4**, wherein from 0.1 to 1.5 acyls are present per active oxygen atoms in said percompound.

15. A method of bleaching textiles at a temperature below 70°C which comprises treating said textiles with an aqueous solution of said solid oxidation compositions for bleaching and washing agents of claim **11** sufficient to supply from 5 to 500 mg per liter of active oxygen.

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