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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{7} :
C11D 1/75, 3/395

A1

(11) International Publication Number: **WO 00/14194**

(43) International Publication Date: 16 March 2000 (16.03.00)

(21) International Application Number: PCT/US99/20846

(22) International Filing Date: 10 September 1999 (10.09.99)

(30) Priority Data:
09/151,042 10 September 1998 (10.09.98) US

(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application
US 09/151,042 (CIP)
Filed on 10 September 1998 (10.09.98)

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(81) Designated States: CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: A STABLE CLEANING FORMULATION CONTAINING AMINE OXIDE AND BLEACHING AGENT

(57) Abstract

Factors causing destabilization and depletion of bleach in formulations made from tertiary amine oxides have been discovered. To overcome such problems, enough hydrogen peroxide is present in an aqueous formulation comprising bleaching agent and tertiary amine oxide to reduce the amount of amine impurity present in the amine oxide product used in forming the mixture. The formulation is provided with water-soluble base (e.g., NaOH) to have a pH of at least about 11, and preferably in the range of 12 to 13.5.

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A STABLE CLEANING FORMULATION CONTAINING AMINE OXIDE AND BLEACHING AGENT

FIELD OF THE INVENTION

This invention concerns stable cleaning formulations which contain both tertiary amine oxide product and a bleaching agent, *e.g.* NaOCl.

BACKGROUND

Tertiary amine oxides have long been recognized as efficacious surfactants in cleaning formulations. Aqueous solutions of tertiary amine oxides have been found to be particularly suitable for use in making liquid cleaning formulations. Commercially available aqueous tertiary amine oxide solutions are typically approximately 30 wt% solutions.

Tertiary amine oxides used in preparing commercial cleaning formulations are always accompanied by impurities, the qualitative identities and quantitative values of which are usually process dependent. For example, most tertiary amine oxides have amine, nitrosoamine and hydrogen peroxide impurities. Metal impurities are also common. The amine impurity typically corresponds to the tertiary amine from which the tertiary amine oxide was prepared, and the amine impurity can be present in an amount of up to about 2 wt%, based on the total weight of tertiary amine oxide, impurities, and water. Usually the tertiary amine oxide concentration amounts to at least 28 wt%, on the same basis. The tertiary amine oxide, its accompanying impurities and water, are hereinafter referred to as tertiary amine oxide product or tertiary amine oxide products to differentiate the combination(s) from the tertiary amine oxide molecule.

The use of bleaching agents in the cleaning formulations is recognized to enhance the formulation's disinfectant qualities. Combining tertiary amine oxide products with the bleaching agents improves the cleaning performance and the viscosity of the formulation.

While the presence of a bleaching agent in the formulations is desirable, it has been noted that the formulation's environment can cause the bleaching agent to become seriously unstable and/or depleted over a short period of time, say, 1 to 10 days. This instability or depletion results in the cleaning formulation losing its high level of disinfectant activity over a short period of time and before it is used by the ultimate consumer. Generally, it is acceptable if the disinfectant activity loss is less than 20% over 6 months at room temperature (15-35°C).

SUMMARY OF THE INVENTION

This invention makes possible the provision of a cleaning formulation which contains tertiary amine oxide product and a bleaching agent in which the bleaching agent is relatively stable and/or is not so readily depleted as in prior art formulations. In addition, this invention provides a process by which such cleaning formulations can be formed. Other features of this invention will become apparent in view of the following description of various embodiments of this invention.

This invention relates to a cleaning formulation which comprises a bleaching agent and tertiary amine oxide product, the bleaching agent and tertiary amine oxide product being in a weight ratio of from 1:3 to 30:1. The tertiary amine oxide product used contains (i) from 28.5 to 32 wt% tertiary amine oxide, (ii) amine impurity, and (iii) hydrogen peroxide in an amount of no more than 0.6 wt%, with the proviso that the amount of hydrogen peroxide that is present is sufficient to reduce the level of amine impurity and thereby increase storage stability of the formulation. In addition, the formulation is provided with a pH within the range of from 11 to 13.5. The cleaning formulations of this invention can sustain less than about a 20% loss of the activity of the bleaching agent in the formulation over a 6-month period when maintained at a temperature within the range of from 15 to 25°C. Most preferably they undergo no more than 5 to 15% loss over a 6-month period at a temperature within the just-recited range.

Also this invention relates to a process for preparing a stable cleaning formulation, which process comprises:

a) forming at least a portion of the formulation from a bleaching agent and a tertiary amine oxide product in a weight ratio of the former to the latter of from 1:3 to 30:1, wherein the tertiary amine oxide product used contains (i) from 28.5 to 32 wt% tertiary amine oxide, (ii) amine impurity, and (iii) hydrogen peroxide in an amount of no more than 0.6 wt%, with the proviso that the amount of hydrogen peroxide that is present is sufficient to reduce the level of amine impurity and thereby increase storage stability of the formulation; and

b) providing the formulation with a pH of at least about 11.

Still another embodiment of this invention is a method of increasing the effective life of an aqueous bleaching solution, which method comprises having in the formulation hydrogen peroxide in an amount of sufficient to reduce the level of amine impurity without depleting the amount of bleaching agent present.

The above and other embodiments of the invention will be still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION

Pursuant to this invention, it has been discovered that there are five main factors affecting the destabilization/depletion of a bleaching agent in a cleaning formulation containing a tertiary amine oxide product. These are: (1) pH of the cleaning formulation, (2) the amount of amine impurities in the product, (3) the amount of hydrogen peroxide impurity in the product, (4) the presence and amount of transition metal ions in the product, and (5) even the amount of tertiary amine oxide product used in the formulation.

The pH of the cleaning formulation must be strongly basic, *i.e.*, it must have a pH of at least about 11. Preferably the pH is within the range of from 12 to 13.5, and most preferably within the range of from 12.2 to 13.

The tertiary amine oxide product can be conventionally produced by the oxidation of a tertiary amine with hydrogen peroxide. See, for example, U.S. 4,247,480, U.S. 4,960,934, U.S. 4,970.340, U.S. 5,055,232, U.S. 5,055,614, U.S. 5,120,469, U.S. 5,164,120, U.S. 5.164.121. U.S. 5,208,374, U.S. 5,292,954, U.S. 5,292,955, U.S. 5,442,113, U.S. 5,498,373, and U.S. 5,498,791, all of which are incorporated herein by reference as if fully set forth. The use of carbon dioxide as a promoter is a preferred technique as it shortens reaction times and, thus, results in an tertiary amine oxide product having less nitrosoamine impurities.

The tertiary amine used in forming the tertiary amine oxide has the formula

$$R_1R_2R_3N$$

wherein R_1 and R_2 are, independently, methyl or ethyl groups and R_3 is an aliphatic, monovalent hydrocarbon group containing in the range of 10 to 14 carbon atoms. C_{12} and C_{14} straight chain alkyl groups are preferred. Preferred are dodecyldimethylamine and tetradecyldimethylamine. Most highly preferred is tetradecyldimethylamine. Between the dodecyl and tetradecyl species, the latter are preferred.

The tertiary amine oxide, which constitutes the major component of the tertiary amine oxide product, can be represented by the formula:

$$R_1R_2R_3N\rightarrow O$$

wherein R_1, R_2 and R_3 are the same as recited above for the tertiary amine reactant. Thus the above comments relative to the preferred R groups for the amine reactant are also applicable to the tertiary amine oxide product. Examples of suitable tertiary amine oxides include decyldimethylamine oxide, undecyldimethylamine oxide, dodecyldimethylamine oxide, tetradecyldiethylamine oxide, dodecylethylmethylamine oxide, tridecyldimethylamine oxide, tetradecyldimethylamine oxide, dodecyldiethylamine oxide, tetradecylethylmethylamine oxide, lauryldimethylamine oxide, myristyldimethylamine oxide, lauryldiethylamine oxide, laurylethylmethylamine oxide, myristylethylmethylamine oxide, myristyldiethylamine oxide, and the like. Amine oxide products containing mixtures of two or more such amine oxides are also suitable. In general, as between the dodecyl and tetradecyl species, the latter are preferred because of their greater effectiveness in the practice of this invention. Of all of the dodecyl species, dodecyldimethylamine oxide is preferred. Of all of the amine oxides, tetradecyldimethylamine oxide is the most highly preferred component as formulations of this invention based thereon have shown the greatest superiority in bleach stability performance.

The tertiary amine and hydrogen peroxide impurities and their amounts in the tertiary amine oxide product are process dependent. There are other impurities which include, one or more of, iron chlorides, nickel chlorides, alkali metal chlorides, especially sodium chloride and magnesium, calcium, titanium, cobalt and copper compounds. The adverse affect on bleaching agent destabilization/depletion can be significant if these other impurities are present in large amounts, which they seldom are. The nickel, iron and alkali metal chlorides are discussed further, *infra*.

It is a significant feature of this invention that the tertiary amine oxide product contain a low level of amine impurity. It is preferred that the amine impurity constitute less than about 0.6 wt% of the tertiary amine oxide product. More preferred tertiary amine oxide products are those which have about 0.2 wt% amine impurity.

The hydrogen peroxide impurity concentration in the tertiary amine oxide product used in preparing the formulation is, in most cases, kept low, say no more than about 0.6 wt%. Hydrogen peroxide reacts with the bleaching agent to deplete it. However, if all other destabilizing and depleting factors are low, it may be permissible and even desirable to have from 0.15 to 1.0 wt% hydrogen peroxide in the tertiary amine oxide product. The desirability arises from the fact that hydrogen peroxide can be beneficial to the color and viscosity qualities of the tertiary amine oxide product used in making the formulation. Thus, if it is desired to have excellent viscosity and color qualities at the expense of some destabilization/depletion of the bleaching agent by hydrogen peroxide, then, it is preferred that the tertiary amine oxide product contain from 0.2 to 0.8 wt% hydrogen peroxide. The foregoing weight percents are based on the total weight of the tertiary amine oxide product.

The hydrogen peroxide concentration in the cleaning formulation can be adjusted downwardly by employing an enzyme, such as catalase, in the formulation. Catalase catalyzes the decomposition of hydrogen peroxide to oxygen and water. Catalase II, which is an enzyme derived from *Corynebact Glutamicum* is preferred over Catalase I, which is derived from cow liver. Catalase I is usually used in an amount of from 50 to 750 ppm depending on the amount of hydrogen peroxide initially present. Catalase II is used in lesser amounts, say 10 to 50 ppm, for a like amount of hydrogen peroxide. The ppm basis is by weight of the tertiary amine oxide product.

The tertiary amine oxide products used in this invention contain no detectable quantity, or at most relatively low amounts, of dissolved Ni or nickel-containing compounds such as $NiCl_2$, and/or dissolved Fe or iron-containing compounds such as $FeCl_3$. Tertiary amine oxide products having from 0 to 1 ppm Ni can be used. The Ni content, if any, is preferably less than about 0.5 ppm and most preferably below 0.4 ppm (wt/wt). The Fe content, if any, is preferably below 1.0 ppm, and most preferably below 0.5 ppm.

In the formulations of this invention that contain 2 wt% of bleach (NaOCl) and 1 wt% of amine oxide, Ni contents of up to 3 ppm and Fe contents of up to 20 ppm are tolerable. These ppm values are based on the weight of the total formulated product, *i.e.*, tertiary amine oxide product plus bleach plus impurities.

The tertiary amine oxide is an antagonist towards the bleaching agent in the cleaning formulation and its use must be moderated. It has been found that a good balance between surfactant function and destabilization/depletion of the bleaching agent is achieved when the weight ratio of the bleaching agent to tertiary amine oxide product is within the range of from 0.33:1 to 30:1, and preferably within the range of from 0.4:1 to 10:1. For dodecyldimethylamine oxide and tetradecyldimethylamine oxide, the weight ratio is preferably within the range of from 0.5:1 to 5:1.

Tertiary amine oxide products useful in this invention can be conveniently produced in accordance with U.S. 4,247,480 or a modification thereof. The modified process entails running the process of U.S. 4,247,480 until the reaction mass contains from 1 to 2.5% of the original amount of tertiary amine reactant fed. Also, at this time, there will be present unreacted hydrogen peroxide and carbon dioxide. The reaction mass temperature is then about 55°C. The reaction mass is then removed from the reactor and allowed to cool to a temperature of from 10 to 35°C. This cooling can occur in a separate process vessel or can occur in drums in which the product will be shipped. If the cooling occurs in the latter, then the drums should be vented to allow for the escape of off-gases. Even though the reaction mass is cool, the reaction continues to occur, all be it at a reduced rate. By the time the tertiary amine oxide product reaches the formulator, which usually takes at least a few days, the reaction is essentially complete. The advantage of using this technique is that there is an attenuation of the formation of nitrosoamines in the product. Significant amounts of nitrosoamines can be produced if the reaction is allowed run to completion or to near completion at the high temperatures taught in U.S. 4,247,480. Also, when running the modified process, it is possible to choose to provide for a sufficient excess of hydrogen peroxide at the beginning of the reaction to obtain the previously discussed 0.15 to 1.0 wt% hydrogen peroxide concentration in the amine oxide product which gives viscosity and color benefits.

The tertiary amine oxide products used in this invention may also be purchased under the trade designations ADMOX® -12 amine oxide and ADMOX® -14 amine oxide from Albemarle Corporation, Baton Rouge, LA. ADMOX-12 amine oxide contains from 28.5 to 32 wt% dodecyldimethylamine oxide, no more than 0.5 wt% dodecyldimethylamine, no more than 0.3 wt% hydrogen peroxide, and from 0 to 1 ppm Ni. ADMOX-14 amine oxide contains from 29 to 31 wt% tetradecyldimethylamine oxide, no more than 0.5 wt% tetradecyldimethylamine, no more than 0.5 wt% hydrogen peroxide, and from 0 to 1 ppm Ni. Herein the term "ppm" is on a weight basis.

Generally the tertiary amine oxide products useful in the cleaning formulations of this invention will have a pH of from 7 to 8 prior to being used in the formulations.

The content of tertiary amine oxide in the cleaning formulations of this invention is typically from 0.2 to 5 wt%.

The cleaning formulations of this invention can also contain constituents other than those described above. For example, the formulations can contain emulsifiers, chelating agents, fragrances, detergents, buffers, viscosifiers, surfactants, abrasives, solvents, and like ingredients. Such other constituents should, of course, be devoid of quantities of amine that would destabilize or deplete the bleach content of the formulation in which the constituents are being used.

The pH of the cleaning formulation can be adjusted by the use of a base such as NaOH, $Mg(OH)_2$, or $Ca(OH)_2$ so as to obtain the before-mentioned requisite value of at least about 11, and preferably in the range of from 12 to 13.5, and most preferably within the range of from 12.2 to 13. The pH of the cleaning formulation is determined by use of an ORION model 290A pH meter. The pH meter is calibrated with buffer solutions with pH = 7 and 10 before each use of the meter. For a dodecyldialkylamine oxide based product, *e.g.*, ADMOX-12 amine oxide, or a tetradecyldialkylamine oxide product, *e.g.*, ADMOX-14 amine oxide, it is preferred that the pH of such products before use in producing the aqueous bleach formulation be within the range of from 7 to 8.

The temperature of the cleaning formulation will have a bearing on the stability/depletion of the bleaching agent. It has been found that it is very beneficent to maintain the cleaning formulation most of the time at a temperature less than 40°C and preferably between 10 and 30°C. Most preferred, is to keep the cleaning formulation at room temperature, say between 18 and 24°C.

The bleaching agents used in the cleaning formulations of this invention are generally provided as aqueous solutions in which the bleaching agent comprises from 1 to 8 wt% and preferably from 1 to 2.5 wt%, the weight percentages being based on the total weight of the solution. Examples of bleaching agents are hypohalites (*e.g.*, sodium hypochlorite (NaOCl), potassium hypochlorite, or sodium hypobromite), haloamines, haloimines, haloamides, haloimides, and the like. Due to its ready availability, NaOCl in a 5 to 5.5 wt% aqueous solution is preferred.

EXAMPLES

The following Examples, wherein all percentages are on an active basis and are based on the total weight of each sample, illustrate the destabilizing/depletion effect that different tertiary amine oxide products have, according to their tertiary amine reactant content, on bleaching agents. A first set of samples was prepared having a pH of 13. These were comprised of 1 wt% sodium hydroxide (for pH adjustment), 2 wt% sodium hypochlorite, 1 wt% tertiary amine oxide product and 96 wt% water. A second set of samples was prepared having a pH of 12 and these samples were comprised of 0.046 wt% sodium hydroxide, 2 wt% sodium hypochlorite, 1 wt% tertiary amine oxide product and 97.954 wt% water. A third set of samples was prepared having a pH of 11. In this case these samples were comprised of 2 wt% sodium hypochlorite, 1 wt% tertiary amine oxide product and 97 wt% water, no sodium hydroxide having been used in making these particular samples. The tertiary amine oxide products used to prepare the samples were:

- ADMOX-12 amine oxide (Albemarle Corporation), (Specification: 31.7 wt% dodecyl dimethyl tertiary amine oxide);
- ADMOX-14 amine oxide (Specification: 30.3 wt% tetradecyl dimethyl tertiary amine oxide);

- BARLOX-12 amine oxide (Lonza Inc.) (Specification: 29.6 wt% lauryl dimethyl tertiary amine oxide);
- BARLOX-14 (Lonza Inc.) (Specification: 31.4 wt% myristyl dimethyl tertiary amine oxide);
- AMMONYX LO (Stephan Co.) (Specification: 30.6 wt% lauryl dimethyl tertiary amine oxide);
- AMMONYX MO (Specification: 30.1 wt% myristyl dimethyl tertiary amine oxide); and
- EMCOL LO (Witco Corp.) (Specification: 30.1 wt% lauryl dimethyl tertiary amine oxide).

Analyses of the tertiary amine oxide products gave the impurity values shown in Table I wherein weight percentage and ppm values are based on the total weight of the tertiary amine oxide solution (which contains about 30 wt% amine oxide).

Table I

Amine Oxide	Fe, ppm	Ni, ppm	Amine, wt%	H_2O_2, wt%
ADMOX-12	<0.5	<0.4	0.00	0.23
ADMOX-14	<0.5	<0.4	0.10	0.6
ADMOX-14	<0.07	<0.3	0.11	0.22
BARLOX 12	2.54	<0.4	0.53	0.07
BARLOX 14	2.59	<0.4	0.56	0.09
AMMONYX LO	<0.5	<0.4	0.45	0.04
AMMONYX MO	2.67	<0.4	0.22	0.0
EMCOL LO	0.11	<0.3	1.82	0.09

The sodium hydroxide used to prepare the samples was from J.T. Baker, 50 wt% aqueous. The sodium hypochlorite was Clorox brand, typically 5.25 wt% active ingredient and was measured each time before use. The water used was distilled and deionized water.

A stock solution of the bleaching agent was prepared by adding 2 grams (if pH=13), 0.092 gram (if pH=12), and zero gram (if pH=11), of the sodium hydroxide (as 50 wt% aqueous solution) and 38.5 grams of the Clorox bleach to 58 grams of the distilled and deionized water. To prepare a sample, the stock solution was then poured into a 4 oz., opaque, plastic bottle. A sufficient amount of a selected tertiary amine oxide product was then added to give a 1 wt% tertiary amine oxide solution. Distilled and deionized water was added to give a 100-gram final sample. The sample was thoroughly mixed for testing. By having a stock solution, each of the samples started with the same amount of bleaching agent. Since NaOCl is sensitive to light and to changes in temperature, the stock bleaching agent solution and samples were stored in the dark at a temperature of 23°C (room temperature).

After each sample was formed from the stock solution and the selected tertiary amine oxide product, its hypochlorite concentration was periodically determined on the following schedule:

Immediately after sample preparation;
Once a week during the first 4 weeks;
Every other week during the next 8 weeks; and
Thereafter once a month until hypochlorite is <1 wt% of sample.

The wt% of the NaOCl of the samples was determined by iodometry using the following procedure: As per the schedule, a 3 to 4 gram sample was weighed into a 250-mL Erlenmeyer flask. To the flask was then added 50 mL of a 55 potassium iodide solution, followed by 25 mL of glacial acetic acid. The resultant solution was then titrated to a brown color with a 0.1 N sodium thiosulfate solution. Then, 5 drops of starch indicator were added and then titration was continued until a colorless endpoint was obtained. The following formula was then used to calculate the wt% of hypochlorite present at the selected time interval:

$$\text{wt\% sodium hypochlorite} = \frac{\text{mLs of sodium thiosulfate used} \times 0.1 \times 0.03772 \times 100}{\text{grams of sample used}}$$

Half-life data from these tests are summarized in Tables II (formulations made using dodecyldimethylamine oxides) and III (formulations made using tetradecyldimethylamine oxides). It can readily be seen from these data that the tertiary amine oxide products used in forming the cleaning formulations of this invention are not nearly as aggressive towards bleaching agents as are other tertiary amine oxide products. Thus, pursuant to this invention it is of great importance to utilize a tertiary amine oxide product having a relatively low amine content in order to significantly reduce destabilization/depletion of bleaching agents with which the tertiary amine oxide product is used. So far as is known, nowhere in the prior art is the effect and significance of amine content on bleach performance of tertiary amine oxides recognized, let alone commented upon.

Table II

Dodecyldimethylamine Oxide	pH	t1/2 (days)
ADMOX 12 amine oxide	13	1768.7
BARLOX 12 amine oxide	13	1262.6
AMMONYX LO amine oxide	13	1585.6
EMCOL LO amine oxide	13	493.6
ADMOX 12 amine oxide	12	93.1
BARLOX 12 amine oxide	12	67.0
AMMONYX LO amine oxide	12	79.1
EMCOL LO amine oxide	12	34.3
ADMOX 12 amine oxide	11	33.0
BARLOX 12 amine oxide	11	31.3
AMMONYX LO amine oxide	11	31.7
EMCOL LO amine oxide	11	22.8

Table III

Tetradecyldimethylamine Oxide	pH	t1/2 (days)
ADMOX 14 amine oxide	13	1883.8
BARLOX 14 amine oxide	13	1186.4
AMMONYX MO amine oxide	13	1391.0
ADMOX 12 amine oxide	12	126.2
BARLOX 12 amine oxide	12	73.8
AMMONYX LO amine oxide	12	86.8
ADMOX 12 amine oxide	11	40.6
BARLOX 12 amine oxide	11	31.0
AMMONYX LO amine oxide	11	36.0

As used herein, the term "water-soluble" means that the material in question has sufficient solubility in water at ambient room temperature to form a solution having a concentration of the material specified herein. Preferably the material will dissolve in still higher amounts in water, but this is not a requirement.

The components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, or solvent). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or formulation as such changes, transformations and/or reactions (*e.g.*, solvation, ionization, or complex formation) are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with forming a desired mixture or in forming a preliminary mixture to be used in forming a desired formulation or product mixture. Even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense (*e.g.*, "comprises" or "is"), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented herein.

THAT WHICH IS CLAIMED IS:

1. A process for preparing a stable aqueous cleaning formulation which process comprises:

a) forming at least a portion of the formulation from a bleaching agent and a tertiary amine oxide product in a weight ratio of the former to the latter of from 1:3 to 30:1, wherein the tertiary amine oxide product used contains (i) from 28.5 to 32 wt% tertiary amine oxide, (ii) amine impurity, and (iii) hydrogen peroxide in an amount of no more than 0.6 wt%, with the proviso that the amount of hydrogen peroxide that is present is sufficient to reduce the level of amine impurity and thereby increase storage stability of the formulation; and

b) providing the formulation with a pH of at least about 11.

2. The process of claim 1 wherein the tertiary amine oxide of the tertiary amine product used is represented by the formula

$$R_1R_2R_3N\rightarrow O$$

wherein R_1 and R_2, are, independently, methyl or ethyl groups and R_3 is an aliphatic, monovalent hydrocarbon group of 10 to 14 carbon atoms.

3. The process of claim 2 wherein the tertiary amine oxide product used contains, if any, no more than 1 ppm (wt/wt) of nickel and no more than 1 ppm (wt/wt) of iron.

4. The process of any of claims 1-3 wherein the bleaching agent is provided as an aqueous solution containing 5 to 5.5 wt% of bleaching agent.

5. The process of any of claims 1-3 wherein the bleaching agent is sodium hypochlorite.

6. The process of any of claims 1-3 wherein the tertiary amine oxide is a dodecyldialkylamine oxide, a tetradecyldialkylamine oxide or a mixture thereof.

7. The process of any of claims 1-3 wherein said pH is in the range of 12 to 13.5.

8. The process of any of claims 1-3 wherein the tertiary amine oxide consists essentially of dodecyldimethylamine oxide or tetradecyldimethylamine oxide or a mixture thereof, wherein the weight ratio of the bleaching agent to the tertiary amine oxide product is from 0.5:1 to 5:1, and wherein the formulation has a pH in the range of 12 to 13.5.

9. The process of any of claims 1-3 wherein the bleaching agent consists essentially of sodium hypochlorite, wherein the tertiary amine oxide consists essentially of

tetradecyldimethylamine oxide, wherein the weight ratio of the bleaching agent to the tertiary amine oxide product is from 0.5:1 to 5:1, and wherein the formulation has a pH in the range of 12 to 13.5.

10. The process of any of claims 1-3 wherein the bleaching agent used is sodium hypochlorite, and wherein the tertiary amine oxide used is an amine oxide product which contains from 28.5 to 32 wt% dodecyldimethylamine oxide, no more than 0.5 wt% dodecyldimethylamine, no more than 0.3 wt% hydrogen peroxide, and from 0 to 1 ppm nickel.

11. The process of any of claims 1-3 wherein the bleaching agent used is sodium hypochlorite, and wherein the tertiary amine oxide used is an amine oxide product which contains from 29 to 31 wt% tetradecyldimethylamine oxide, no more than 0.5 wt% dodecyldimethylamine, no more than 0.3 wt% hydrogen peroxide, and from 0 to 1 ppm nickel.

12. The process of claim 10 wherein said pH is in the range of from 12 to 13.5.

13. The process of claim 11 wherein said pH is in the range of from 12 to 13.5.

14. An aqueous cleaning formulation comprising at least a bleaching agent and a tertiary amine oxide wherein at least a portion of the formulation is formed from a bleaching agent and a tertiary amine oxide product in a weight ratio of the former to the latter of from 1:3 to 30:1, wherein the tertiary amine oxide product used contains (i) from 28.5 to 32 wt% tertiary amine oxide, (ii) amine impurity, and (iii) hydrogen peroxide in an amount of no more than 0.6 wt%, with the proviso that the amount of hydrogen peroxide that is present is sufficient to reduce the level of amine impurity and thereby increase storage stability of the formulation; said formulation having a pH of at least about 11.

15. A formulation of claim 14 wherein the tertiary amine oxide of the tertiary amine product used is represented by the formula

$$R_1R_2R_3N\rightarrow O$$

wherein R_1 and R_2, are, independently, methyl or ethyl groups and R_3 is an aliphatic, monovalent hydrocarbon group of 10 to 14 carbon atoms.

16. A formulation of claim 14 wherein the tertiary amine oxide product used contains, if any, no more than 1 ppm (wt/wt) of nickel and no more than 1 ppm (wt/wt) of iron.

17. A formulation of any of claims 14-16 wherein the bleaching agent is sodium hypochlorite.

18. A formulation of any of claims 14-16 wherein the bleaching agent is provided as an aqueous solution containing 5 to 5.5 wt% of bleaching agent.

19. A formulation of claim 18 wherein the bleaching agent is sodium hypochlorite.

20. A formulation of any of claims 14-16 wherein the tertiary amine oxide is a dodecyldialkylamine oxide, a tetradecyldialkylamine oxide or a mixture thereof.

21. A formulation of any of claims 14-16 wherein said pH is in the range of 12 to 13.5.

22. A formulation of any of claims 14-16 wherein the tertiary amine oxide consists essentially of dodecyldimethylamine oxide or tetradecyldimethylamine oxide or a mixture thereof, and wherein the weight ratio of the bleaching agent to the tertiary amine oxide product is from 0.5:1 to 5:1.

23. A formulation of any of claims 14-16 wherein the bleaching agent consists essentially of sodium hypochlorite, and wherein the tertiary amine oxide consists essentially of tetradecyldimethylamine oxide.

24. A formulation of any of claims 14-16 wherein the bleaching agent used is sodium hypochlorite, and wherein the tertiary amine oxide used is an amine oxide product which contains from 28.5 to 32 wt% dodecyldimethylamine oxide, no more than 0.5 wt% dodecyldimethylamine, no more than 0.3 wt% hydrogen peroxide, and from 0 to 1 ppm nickel.

25. A formulation of any of claims 14-16 wherein the bleaching agent used is sodium hypochlorite, and wherein the tertiary amine oxide product used contains from 29 to 31 wt% tetradecyldimethylamine oxide, no more than 0.5 wt% dodecyldimethylamine, no more than 0.3 wt% hydrogen peroxide, and from 0 to 1 ppm nickel.

26. A formulation of claim 24 wherein said pH is in the range of from 12 to 13.5.

27. A formulation of claim 25 wherein said pH is in the range of from 12 to 13.5.

28. A method of increasing the effective life of an aqueous bleaching formulation formed from (i) a tertiary amine oxide product containing amine impurity, and (ii) a bleaching agent, which method comprises having in the formulation hydrogen peroxide in an amount sufficient to reduce the level of amine impurity without depleting the amount of bleaching agent present.

29. A method of claim 28 wherein the tertiary amine oxide of the tertiary amine product used is represented by the formula

$$R_1R_2R_3N\rightarrow O$$

wherein R_1 and R_2, are, independently, methyl or ethyl groups and R_3 is an aliphatic, monovalent hydrocarbon group of 10 to 14 carbon atoms.

30. The process of claim 28 or 29 wherein the tertiary amine oxide product used contains, if any, no more than 1 ppm (wt/wt) of nickel and no more than 1 ppm (wt/wt) of iron.

INTERNATIONAL SEARCH REPORT

Intern   nal Application No
PCT/US 99/20846

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C11D1/75   C11D3/395

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C11D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 839 077 A (CRAMER RANDALL J ET AL) 13 June 1989 (1989-06-13) column 7, line 61 -column 8, line 6 column 9, line 55 - line 59 tables 1-5 claims 1-13 ---	1-30
X	EP 0 206 534 A (CLOROX CO) 30 December 1986 (1986-12-30) examples 1-12,17-19 page 16, line 12 - line 17 ---	1-30
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search
7 January 2000

Date of mailing of the international search report
17/01/2000

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INTERNATIONAL SEARCH REPORT

Inter: nal Application No
PCT/US 99/20846

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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