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PROCESS FOR PREPARATION OF A BLEACHING AGENT

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1 Claim. (Cl. 252—186)

This application is a continuation-in-part of U.S. patent application Serial Number 775,683, filed November 24, 1958, in the names of the present inventors, now abandoned.

This invention relates to a process of preparing bleach solutions which contain organic peracids in high concentration, which solutions are highly stable and therefore are particularly suited to being stored for use at a desired time. These bleach solutions are suitable for bleaching textile fibers in the form of loose fiber material as well as of spun, woven and knitted products consisting of native and artificial fibers of cellulose or of synthetic fibers, and of pulp or pulp products.

The bleaching processes known at the present time have the disadvantage that they deteriorate the various fiber materials in a higher or lower degree, or as in the chlorite bleach, develop highly toxic fumes, and destroy the materials of construction employed, particularly stainless steels. Most of these bleaching processes require a highly alkaline pretreatment or are carried out themselves in alkaline solutions which cause an undesired change in the textile properties of the fiber materials and promote a deterioration of these fiber materials by molecular and atomic oxygen. Another disadvantage of most of the previous bleaching processes resides in that a large number of even fast dyestuffs of the vat and naphthol types are varied in hue or in their fastness properties by the bleach and only a relatively small number of these dyestuffs were suitable for dyeing articles to be bleached articles so that the field of application of the bleaching of dyed articles was highly restricted and increased in cost.

It is known that organic peracids, such as monoperacetic acid, have a bleaching activity even in acid solutions and the bleach carried out with these solutions does not have the above-mentioned disadvantages and that monoperacetic acid is highly suitable for bleaching fabrics which contain vat- or naphthol-dyed effects. The direct use of monoperacetic acid for bleaching, however, involves very great difficulties because the same cannot be used on a large scale owing to its relatively high cost and the danger of explosion inherent in highly concentrated solutions thereof.

For bleaching with peracids it has been necessary therefore, to form them in the bleach solutions by the action of hydrogen peroxide or other peroxides on the corresponding acids or acid anhydrides. A number of processes are known in which peracids are formed in concentrated or dilute solutions. These processes have not been successful because of the small yields and the danger involved. For instance, peracetic acid can be obtained by the action of concentrated solutions of hydrogen peroxide on acetic anhydride in the presence of sulfuric acid or acid salts. This leads to sudden, high temperature rise and spontaneous decomposition. For this reason this process is not suitable for bleaching plants. It is also known that peracids or their salts can be obtained by the action of the peroxide solution on alkaline solutions of anhydrides of organic acids. This reaction is successful only at a relatively high pH, preferably between 8 and 11, and in dilute solutions. For higher concentrations at these pH's, that is above about 12 volumes or 3.5% of active oxygen expressed as hydrogen peroxide, solutions such as are used for replenishing used bleach solutions, or for continuous bleaching in vessels with a prolonged heat treatment, this method of preparing bleach solutions is not applicable owing to excessive losses of active oxygen.

The use of higher active oxygen content solutions, those containing on the order of about 4 to 10% of active oxygen expressed as hydrogen peroxide or 2% as peracetic acid, is of great importance, since the fibers must be saturated with bleach solution, and in contacting the wetted fibers with bleach, the concentration of the bleach solution is reduced. Thus, starting with a bleach solution containing peracetic acid in the amount of about 2 to 3.5%, that is an amount of active oxygen corresponding to that in 4 to 7% of hydrogen peroxide, the bleach bath is diluted to a point where it contains only about 0.5% of peracetic acid, which corresponds to about 1% of hydrogen peroxide on an active oxygen basis. This is the amount which typically, actually is required for bleaching. Use of a peracetic acid bleach solution having an excessive pH involves also deterioration of the fiber during bleaching, and is necessary in this process to reduce the pH by an addition of acids to the value required for bleaching with peracids. This involves an additional consumption of acids, in cases where the pH is on the order of 8 to 11.

It is a feature of this invention to provide aqueous peracetic acid solutions for the bleaching of fibers in which the solutions have a high active oxygen content, yet are stable against decomposition of the active oxygen even when the solutions are prepared for use as much as a day or more before they are used.

It has now been found, quite surprisingly, that such stable peracetic acid solutions, having an active oxygen concentration of at least 12 volumes (3.5% expressed as hydrogen peroxide, or 1.75% expressed as peracetic acid), can be prepared from hydrogen peroxide and acetic anhydride by reacting these reagents in an aqueous medium at a pH of about 2 to no greater than about 4, in the presence of ammonium ions introduced in the form of ammonia, ammonium hydroxide, or organic, primary, secondary or tertiary amine bases such as pyridine, monoethanolamine, triethanolamine, and the like. The action of these additives does not only depend on their basic character, which enables them to substitute alkali, but also on their pronounced catalytic activity, whereby the ion equilibrium of the mixed solution is displaced toward the peracetic acid which is being formed. This displacement of the ion equilibrium takes place readily not only at pH-values above 8, as with other alkalies, but is also achieved with pH values in the low ranges of 2 to 4. Furthermore, the peracetic acid formed is stable at a pH in this range. It has been observed that the pH of the solution is adjusted within a few seconds to a final value, whereas the formation of peracetic acid does not begin immediately because a considerable amount of organic peroxide is formed first, which splits to form peracetic acid only after the reaction has proceeded for some time. The bleach solutions thus obtained exhibit a particularly good bleaching activity particularly on native cellulose fibers. It is believed that the presence of ammonium bases has a favorable effect on the bleaching process and assists particularly in the removal of the natural waxes.

The ratio between the peractic acid formed and the nonreacted hydrogen peroxide still in solution can be determined by titration with potassium permanganate and subsequent addition of potassium thiosulfate. Favorable bleaching results will be obtained if at least 65% of the hydrogen peroxide used is reacted to form peracetic acid. The bleaching activity of the solutions is appreciably re-

duced if the peracetic acid content is below this value. According to the process of the invention, it is possible, however, to obtain almost complete reaction of the hydrogen peroxide to form peracetic acid when the said additives are present. It has been found that native and artificial cellulose fibers can be bleached with these solutions without chemical deterioration of the cellulose if the content of non-reacted hydrogen peroxide does not exceed 35% of the hydrogen peroxide charged. The determination of the degree of fluidity has shown that the same is not appreciably higher than before the treatment.

The solutions have given satisfactory results in the bleaching of materials dyed with almost all known vat or naphthol dyestuffs without causing changes in the hue of fastness of these dyestuffs. The bleach solutions prepared according to the invention may be used in practically all conventional bleaching apparatus. Acid-resisting materials such as ceramics, synthetic resins and particularly stainless steels may be used as maerials of construction particularly of those parts of such apparatus which are contacted by the bleach solution. Such materials are not attacked by these bleach solutions. It has been found that the optimum bleaching temperature is in the range of 60–90° C., although temperatures as low as about 25° C. can be used if the solution has a high active oxygen concentration, e.g., at least about 4 to 5% expressed as hydrogen peroxide. The vessels in which the bleach is performed are suitably closed against the environment or covered because peracetic acid is somewhat volatile at these temperatures.

The optimum pH-value for bleaching depends on the material to be bleached. A preferred range is between 4.5 and 6, and the present solutions can be brought to this level by addition of phosphate, particularly tetrasodium pyrophosphate, or other alkali to the bleaching solution. Addition of phosphates also avoids undesirable catalytic effects and a contamination of the material to be bleached, or of the process water, with iron, manganese and copper.

The bleaching operation will normally be conducted with the present peracetic acid solutions containing active oxygen in an amount corresponding to that in about 1% of hydrogen peroxide; this amounts to about 0.5% of peracetic acid. The amount of active oxygen, can however, be as much as 4 to 5% expressed as hydrogen peroxide, or 2 to 2.5% expressed as peracetic acid, if bleaching temperatures are not permitted to exceed about 25° to 35° C. Intermediate concentrations of active oxygen wll be employed with temperatures intermediate the 25° C. to 35° C. range and the 60° to 90° C. range.

The bleach solutions may be directly prepared in the concentrations required for bleaching, in accordance with the following examples, or in a concentrated form for replenishing used bleach liquors or as stock solution for a quick preparation of bleach liquors. The concentrated stock solutions may contain active oxygen in a concentration of up to about 10% as hydrogen peroxide, or 5% as peracetic acid. More highly concentrated solutions tend toward instability. It is suitable to preclean the material to be bleached and to remove any size from woven fabric by a desizing treatment. A pretreatment with strong caustic alkali baths, as is usual for bleaching native cellulosic fibers, can be employed but is not essential unless bleaching to pure white is desired. It is also possible to apply a weak treatment with other bleaching agents, such as sodium hypochlorite, before or after bleaching with the present bleach solution. This weak treatment may be carried out in a concentration which is so low that it does not cause a deterioration of the fiber material.

The following examples illustrate the invention, but the latter is not limited thereto.

Example 1

A peracetic acid solution suitable for use directly as a bleach solution, or dilutable to form a more dilute bleach solution, was prepared by mixing the following ingredients. The temperature of the reaction mixture rose to about 171° F. during the reaction.

	Ml.
Water	224
Ammonium hydroxide (30% as NH_3)	41
Hydrogen peroxide, 35% by weight	348
Acetic anhydride	387

The solution reached a final pH of about 3.1.

The following percentages of the added hydrogen peroxide reacted:

	Percent
After 15 minutes	81.5
After 60 minutes	86.1
After 120 minutes	86.5

Ninety-three percent of the peracetic acid formed was retained after 24 hours, whereas a similar solution at pH 5,5, containing the amount of ammonium hydroxide required to provide that pH, retained only 5% or less of the peracetic acid after storage for a 24-hour period. Storage in both cases was at 24° C.

Example 2

The procedure of Example 1 was followed, with the temperature of the solution on mixing of the following ingredients reaching 146° F.

	Ml.
Water	388
Ammonium hydroxide (30% as NH_3)	35
Hydrogen peroxide, 35% by weight	260
Acetic anhydride	317

The solution reached a final pH of about 3.3.

The following percentages of the added hydrogen peroxide reacted:

	Percent
After 15 minutes	90.4
After 60 minutes	93.4
After 120 minutes	92.9

Eighty-nine percent of the peracetic acid formed was retained after storage for 24 hours at 24° C., whereas a similar solution containing sufficient ammonium hydroxide to create a pH of 5.5, retained only up to about 10% of the peracetic acid formed after storage for 24 hours at 24° C.

Example 3

The procedure of Example 1 was followed, with the temperature of the solution on mixing of the following ingredients reaching 121° F.

	Ml.
Water	508
Ammonium hydroxide (30% as NH_3)	30
Hydrogen peroxide, 35% by weight	206
Acetic anhydride	256

The solution reached a final pH of 3.6.

The following percentages of the added hydrogen peroxide reacted:

	Percent
After 15 minutes	91.1
After 60 minutes	93.8
After 120 minutes	92.9

Ninety percent of the peracetic acid formed was retained after storage for 24 hours at 24° C., whereas a similar solution containing sufficient ammonium hydroxide to create a pH of 5.5 retained only about 25% of the peracetic acid formed after similar storage.

Example 4

The procedure of Example 1 was followed with the temperature of the solution on mixing of the following ingredients reaching 106° F.

	Ml.
Water	637
Ammonium hydroxide (30% as NH_3)	35
Hydrogen peroxide, 35% by weight	146
Acetic anhydride	182

The solution reached a final pH of 3.9.

The following percentages of the added hydrogen peroxide reacted:

	Percent
After 15 minutes	90
After 60 minutes	94
After 120 minutes	94.1

After 24 hours storage at 24° C., 80% of the peracetic acid formed was retained, whereas when a similar solution was prepared at pH 5.5 with an amount of ammonium hydroxide required to provide that pH, only about 40% of the peracetic acid formed was retained, after storage under similar conditions for similar times.

Example 5

Water	liters	67
Ice	kg	10
Monoethanolamine	kg	0.75
Hydrogen peroxide, 35% by weight	liters	10
Acetic anhydride	do	12.5

Ice is added to the above reaction mixture to prevent a temperature rise above 35° C. Alternatively, the mixture may be cooled by means of cooling pipe coils.

The following percentages of the added hydrogen peroxide reacted:

	Percent
After 30 minutes	45
After 60 minutes	63
After 90 minutes	68
After 120 minutes	71
After 300 minutes	73

The solution is ready for use after a reaction time of about 3 hours.

Example 6

Water	liters	67
Ice	kg	10
Triethanolamine	kg	0.9
Hydrogen peroxide, 35% by weight	liters	10
Acetic anhydride	do	12.5

The pH value of the finished solution is 2.7.

The following percentages of the added hydrogen peroxide reacted:

	Percent
After 30 minutes	36
After 60 minutes	50
After 90 minutes	58
After 120 minutes	63
After 300 minutes	68

Example 7

	Liters
Cold water	63
Pyridine	1
Hydrogen peroxide, 35% by weight	16
Acetic anhydride	20

A special cooling of this reaction mixture is not necessary where water at less than 12° C. is available. The pH-value of the finished solution is 2.7.

The following percentages of the added hydrogen peroxide reacted:

	Percent
After 30 minutes	63
After 60 minutes	70
After 90 minutes	72
After 120 minutes	72
After 300 minutes	77

The bleaching agent solutions described in Examples 5, 6, and 7 are concentrated stock solutions, which are durable for two or three days and may be used for bleaching in the following manner:

One hundred kilograms of knitware of polyamide fiber material are placed into a circulating device of stainless steel and treated with a solution to which 10 liters of a stock solution according to Example 5 or Example 6 or 5 liters of a stock solution according to Example 7 have been added. Because these solutions have a low pH-value, sodium pyrophosphate or, if desired, some caustic soda is added to the solution to raise the pH-value of the solution to 4.5–5. The bleach solution thus prepared is caused to circulate at a temperature of 60–90° C., through the material to be bleached. The bleaching is effected within one to two hours at a temperature of 60–90° C. This is followed by warm and cold rinsing and drying. Other fiber materials such as linen, regenerated cellulose, rayon, pulp and pulp products etc., may be bleached with similar success.

We claim:

A process of preparing a stable, concentrated aqueous solution of a bleaching agent containing monoperacetic acid for bleaching fiber materials, which comprises reacting hydrogen peroxide and acetic anhydride in an aqueous medium in the presence of ammonium hydroxide, said hydrogen peroxide being employed in an amount which provides an active oxygen content of at least 12 volumes in said bleaching agent solution, and said ammonium hydroxide and acetic anhydride being present in amounts which provide a pH of 2 to 4 in said bleaching agent solution, and carrying out the reaction until no more than 35% of the hydrogen peroxide introduced is present as hydrogen peroxide, and at least 65% of the introduced hydrogen peroxide has reacted with said acetic anhydride to form monoperacetic acid.

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