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HAIR BLEACHING COMPOSITIONS AND PROCESS

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ABSTRACT OF THE DISCLOSURE

Hair bleaching compositions containing barbituric acid, certain derivatives of barbituric acid or certain salts of barbituric acid and derivatives thereof, and a peroxygen compound as essenital components, said compositions having a pH in a range of from about 8 to about 11, and hair bleaching process.

BACKGROUND OF THE INVENTION

This invention relates to hair bleaching compositions containing a barbituric acid compound as the characterizing ingredient.

Bleaching compositions used on hair differ from those used with textiles, fabrics, in hard surface cleansing and the like in that hair bleaching compositions, in addition to oxidizing and destroying the colored melanin of the hair, must be suitable for use in contact with the human skin and must not damage the hair excessively. Furthermore, since hair bleaches are a member of the class of materials known as cosmetics, it is desirable that they be aesthetically acceptable to the user. Finally, it is desirable that a hair bleaching composition remove the melanin coloration from the hair as quickly as possible, both for the sake of convenience and to help prevent untoward damage to the hair and irritation to the skin and scalp. Most current bleaching systems require exposure to the hair for periods of from about 2 to 5 hours, depending upon the desired degree of bleaching. Such long periods of exposure frequently result in irritation to the skin and some damage to the hair.

Hair bleaches commonly consist of a peroxide oxidizing agent, bleach enhancing agents, and a variety of additional cosmetic and bleach stabilizing agents. Oxidizing agents such as the various hypochlorites and halogenated cyanuric acid compounds suitable for use on hard surfaces and in fabric bleaching are not suitable for use on hair since they are too damaging and too irritating to the skin. Peroxide bleaches used on hair must be "activated," this being accomplished by the use of an "activating" agent to adjust the pH to a basic range. The most common material for adjusting the pH of peroxide hair bleaching compositions is an aqueous solution of ammonia, commonly referred to as ammonium hydroxide.

In addition to ammonium hydroxide, a variety of other activating and/or enhancing agents have been suggested for use in hair bleaching compositions. U.S. Pat. 2,283,350, granted May 19, 1942 to N. Baum, discloses the use of aliphatic amines and hydroxyaliphatic amines as substitutes for ammonium hydroxide in hair bleaching compositions. Moreover, U.S. application Ser. No. 129,554, filed Mar. 30, 1971 by Knohl and Zeffren, entitled "Hair Bleaching Compositions and Process," discloses hair bleaches containing arginine and various arginine-containing proteins. Another U.S. application, Ser. No. 129,555, filed Mar. 30, 1971 by Knohl and Zeffren, entitled "Hair Bleaching Composition and Process," discloses hair bleaches containing guanidine compounds which eliminate the need for ammonium hydroxide thereby providing a bleaching composition having essentially no odor or skin irritation which is attributable to ammonium hydroxide.

The use of guanidine compounds in place of ammonium hydroxide is a preferred embodiment of the present invention and will be discussed more fully hereinafter. This patent and these applications are incorporated herein by reference.

As discussed briefly above, current bleaching systems and processes inevitably cause some damage to the hair and this damage is usually attributed to the oxidation of cystine bonds in the hair polymer. This cystine oxidation damage is increased by higher peroxide concentrations in the bleach and by longer contact times of said bleach with the hair. It has been unexpectedly found that the use of the barbituric acid compounds of the present invention result in superior bleaching characteristics, while permitting the use of significantly lower amounts of bleaching actives thereby causing less skin irritation and hair damage. Further, the compounds of the present invention result in considerably shorter bleaching times, further diminishing skin irritation and hair damage.

THE PRIOR ART

A variety of "activating" and/or enhancing agents for peroxygen compounds are known in the art. See, for example, U.S. 3,338,839 to MacKeller et al., which issued on Aug. 29, 1967. Other compositions are disclosed in U.S. 2,955,905 to Davies et al., which issued Oct. 11, 1960; and U.S. 3,177,148 to Bright et al., which issued on Apr. 6, 1965. However, the prior art does not disclose the barbituric acid compounds of the present invention or their use in hair bleaching compositions.

Accordingly, it is an object of the present invention to provide improved peroxygen bleaching compositions containing barbituric acid, certain derivatives of barbituric acid and certain salts of barbituric acid, and derivatives thereof of the type hereinafter disclosed.

It is another object of the present invention to provide hair bleaching compositions which are faster acting and less damaging than known hair bleaches.

It is yet another object of the present invention to provide improved bleaching compositions which are more aesthetically pleasing. These and other objects are obtained by the present invention as will become apparent from the following disclosure.

SUMMARY OF THE INVENTION

It has been surprisingly found that barbituric acid, certain derivatives of barbituric acid, certain salts of barbituric acid and said derivatives such as those discussed more fully hereinafter, when combined with a peroxygen compound, wherein the pH of the composition ready for use is from about 8 to about 11, preferably from about 9 to about 10, markedly improve the speed of bleaching and in the preferred compositions described hereinafter make possible the use of about ½ the peroxygen concentration currently used while greatly decreasing the time necessary for bleaching. Heretofore, it was necessary to bleach the hair for about 2 to about 5 hours, depending upon the degree of bleaching desired. The present invention makes it possible to get desirable bleaching action in from about ½ hour to about 2 hours, depending upon the level of bleaching desired. The lower concentration of peroxygen compound plus the greatly decreased time necessary for bleaching to be accomplished results in less skin irritation and less damage to the hair. In addition, it results in a more aesthetically pleasing and convenient composition.

While not intending to be restricted by theory, it is hypothesized that the barbituric acid compounds of the present invention react with the peroxygen compound to form a compound which penetrates the hair shaft more rapidly and/or causes an increased reaction rate of melanin bleaching. Whatever the reason for the improved

hair bleaching activity of the present compositions, the improvement is not attributable to the pH, but is related to the presence of the barbituric acid compounds.

In addition to the above essential components, the bleaching compositions of the present invention may contain as a preferred embodiment certain bleach enhancing agents more fully defined hereinafter.

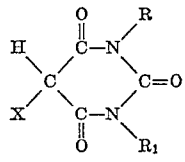
In addition to the above compounds, the bleaching compositions of the present invention may also contain additional agents such as buffers, thickeners, perfumes and other minor ingredients to make the composition more aesthetically pleasing.

In addition, this invention encompasses a process for bleaching hair, especially growing human hair, which comprises contacting said hair with a composition comprising as essential components a peroxygen compound and a barbituric acid compound, the pH of said composition being in the range of from about 8 to about 11.

DETAILED DESCRIPTION OF THE INVENTION

The barbituric acid compounds used herein include those having the formula:

(I)



wherein R and R_1 are the same or different and are selected from the group consisting of: hydrogen; alkyl groups of from about 1 to about 6 carbon atoms; hydroxyalkyl groups of from about 1 to about 6 carbon atoms; carboxyalkyl groups of from about 1 to about 6 carbon atoms; aryl groups of from about 6 to about 12 carbon atoms, for example, phenyl, biphenyl, and naphthyl; and aralkyl groups of from about 6 to about 14 carbon atoms, for example, benzyl, paraethylphenyl and 2-phenylethyl; and X is selected from the group consisting of hydrogen, sodium, potassium and ammonium.

The term "aralkyl" as used herein means any alkyl-aryl combination within the defined limits, for example, alkaryl and alkaralkyl.

Examples of compounds as defined in formula (I) above include:

barbituric acid;
N-methylbarbituric acid;
N-ethylbarbituric acid;
N-isopropylbarbituric acid;
N-2-methylphentylbarbituric acid;
N,N'-dimethylbarbituric acid;
N,N'-diisopropylbarbituric acid;
N-methyl-N'-isopropylbarbituric acid;
N-isopropyl-N'-hexylbarbituric acid;
N-methyl-N'-hydroxymethylbarbituric acid;
N,N'-bis(hydroxymethyl)barbituric acid;
N,N'-bis(β-hydroxyethyl)barbituric acid;
N-ethyl-N'-6-hydroxyhexylbarbituric acid;
N-methyl-N'-carboxymethylbarbituric acid;
N,N'-bis(carboxymethyl)barbituric acid;
N,N'-bis(carboxypropyl)barbituric acid;
N-propyl-N'-5-carboxypentylbarbituric acid;
N,N'-diphenylbarbituric acid;
N,N'-dinaphthylbarbituric acid;
N,N'-bis(biphenylyl)barbituric acid;
N-phenyl-N'-naphthylbarbituric acid;
N-methyl-N'-phenylbarbituric acid;
N-hydroxyethyl-N'-naphthylbarbituric acid;
N-carboxymethyl-N'-biphenylylbarbituric acid;
N,N'-bis(benzyl)barbituric acid;
N-methyl-N'-benzylbarbituric acid;
N-benzyl-N'-hydroxyethylbarbituric acid;
N-methyl-N'-paraethylphenylbarbituric acid;
N,N'-bis(2-phenylethyl)barbituric acid;

and the sodium, potassium and ammonium salts of the above named compounds.

The above compositions are all readily available or can be readily prepared utilizing known laboratory procedures which involve the condensation of a urea derivative with malonic acid.

The bleaching compositions of the present invention comprises:

(A) from about 0.1% to about 10%, preferably from about 0.8% to about 3%, by weight of a barbituric acid compound of formula (I) as defined above;
(B) from about 1% to about 10%, preferably from about 2% to about 6%, by weight of a water-soluble peroxygen compound which yields hydrogen peroxide in solution; and
(C) from about 0% to about 98.9% of an inert diluent.

Suitable peroxygen compounds for use in the compositions and process of the present invention include: hydrogen peroxide, any of the water-soluble alkali metal peroxides, e.g., sodium and potassium peroxide, etc.; alkaline earth metal peroxides; peroxide complexes such as the water-soluble addition compounds of materials such as urea and guanidine with hydrogen peroxide, e.g., urea peroxide, guanidine peroxide, and the like; organic peracids; organic hydroxyperoxides; and inorganic peroxygen salts such as perborates, such as sodium perborate, persilicates, percarbonates, perphosphates and perpyrophosphates.

Preferred peroxygen compounds for use in the compositions of the present invention are those which yield hydrogen peroxide in solution. Such compounds include hydrogen peroxide, the water-soluble alkali metal peroxides, the alkaline earth metal peroxides, the water-soluble peroxide complexes such as urea peroxide and the like, the perborates, such as sodium perborate, and the percarbonates, such as potassium percarbonate. Most preferred for use in the compositions of the present invention are hydrogen peroxide, urea peroxide, and sodium perborate.

The peroxygen component of the bleaches described herein usually comprises from about 1% to about 10% by weight of the total composition. A peroxygen concentration of from about 2% to about 6% by weight is most preferred.

Examples of inert diluents are any of the liquid and solid compositions commonly used in the art which do not interfere with the bleaching process and are not irritating to the scalp and/or damaging to the hair. Examples of liquid diluents include, but are not limited to, water, lower alcohols, for example, ethanol, isopropyl alcohol, ethylene glycol, propylene glycol, 1,3-propanediol, glycerine, and mixtures thereof. Examples of solid diluents include, but are not limited to, starch, sodium chloride, sodium sulfate, cellulose, amorphous silicates, and the like.

In addition to the components described, the compositions of the present invention may also contain as a preferred embodiment one or more of certain bleach enhancing agents in amounts of from about 0.1% to about 45% by weight. One example of such a bleach enhancing agent is amonium hydroxide which can be present in amounts of from about 0.1% to about 25%, preferably from about 2% to about 10%.

Other bleach enhancing agents which may be utilized in the present invention include agents such as ammonium peroxydisulfate or alkali metal peroxydisulfates or any of the other common peroxygen salts commonly used in hair bleaching compositions such as the ammonium or alkali metal peroxydiphosphates described in South African Patent Application 692,638, published Nov. 26, 1969, to B. Cohen. Mixtures of any of the foregoing enhancing agents are also suitable. These enhancing agents are preferably each used at a concentration of

from about 1% to about 10%, most preferably from about 3% to about 8% by weight. Ammonium peroxydisulfate, the potassium and sodium peroxydisulfates, and potassium peroxydiphosphate are preferred agents of this type.

Another example of preferred bleach enhancing agents for use in the compositions of the present invention includes certain guanidine compounds.

The guanidine compounds used herein include guanidine and its basic derivatives, as well as the reaction products of these compounds with an acid, i.e., guanidinium salts. Such basic compounds and salts are referred to collectively herein as "guanidine compounds." Compounds such as guanidine, monoalkyl-guanidines, dialkyl-, trialkyl-, and tetraalkyl-guanidines having alkyl substituents on each amine nitrogen atom, aryl-guanidines of the same type, especially N,N'-diphenylguanidines, and the like all can be suitably employed *per se* or neutralized with acids of the type hereinafter disclosed to form soluble guanidinium salts which are suitably employed in the bleaching compositions of this invention. For example, guanidine, N-phenylguanidine, N-methylguanidine, N-butylguanidine, N,N'-diphenylguanidine, N-phenyl-N'-hexylguanidine, N-hydroxyethylguanidine, N,N,N', N'-tetraethylguanidine, N,N'-dihydroxymethylguanidine, N,N-diphenyl-N'-hydroxybutylguanidine, and the like can be used *per se* or can be treated with an acid of the type hereinafter disclosed to prepare guanidinium salts suitable and preferred for use herein. Guanidine and the substituted guanidine compounds are commercially available materials.

Acids which can be reacted with guanidine and the basic derivatives thereof to provide guanidinium salts suitable for use in the bleaching compositions of this invention include those acids having anions which are compatible with peroxides, especially hydrogen peroxide. For example, mineral acids such as hydrochloric acid, phosphoric acid, carbonic acid, sulfuric acid, nitric acid, and the organic acids such as formic acid, acetic acid, lauric acid, chloroacetic acid and the like are all suitable for this use. Acids containing metallo-anions and strongly reducing anions, e.g., chromic acid and hydrogen thiocyanate, are not suitable herein in that these anions react with the peroxide.

Reaction of the aforementioned guanidine and derivatives thereof with the exemplary acids in the appropriate amounts yields the guanidinium salts useful herein. For example, guanidinium chloride, guanidinium carbonate, guanidinium sulfate, N-methylguanidinium sulfate, N-decylguanidinium hydrochloride, N-methoxyguanidinium phosphate, N-hydroxymethyl-N'-hydroxyethylguanidinium carbonate, N-phenylguanidinium carbonate, N-phenylguanidinium chloride, N-phenyl-N'-hexylguanidinium hydrochloride, guanidinium phosphate, guanidinium pyrophosphate, guanidinium nitrate, guanidinium acetate, guanidinium chloroacetate and the like, are suitable for use in the compositions of this invention. The carbonates and phosphates are preferred for this purpose in that they are self-buffering. Guanidinium chloride, guanidinium phosphate and guanidinium carbonate are especially preferred for use herein in amounts of from about 2% to about 10% by weight.

As noted heretofore the various bleach enhancing agents can be used singly or in mixtures thereof. For the purpose of the present invention, a preferred guanidinium compound or combination with a preferred ammonium peroxydisulfate or an alkali metal peroxydisulfate is most preferred.

For example, a preferred composition embodying the present invention is as follows:

(A) from about 0.8% to about 3% by weight of barbituric acid;

(B) from about 2% to about 6% by weight of a water-soluble peroxygen compound selected from the group consisting of hydrogen peroxide, sodium perborate, and urea peroxide;

(C) from about 3% to about 8% by weight of a bleach enhancing agent selected from the group consisting of ammonium peroxydisulfate, potassium peroxydisulfate, sodium peroxydisulfate, potassium peroxydiphosphate, and mixtures thereof;

(D) from about 2% to about 10% by weight of a bleach enhancing agent selected from the group consisting of guanidinium carbonate, guanidinium chloride and guanidinium phosphate and mixtures thereof; and

(E) balance, water.

As noted hereinabove, peroxygen containing hair bleaches are used in the basic pH range of from about 8 to about 11. During the course of the hair bleaching operation, the pH of the bleach solution will sometimes change; therefore, in a preferred embodiment of this invention, a buffer is included in the composition to maintain a relatively constant pH within the desired range. Any of the common peroxide-stable buffers suitable for use in the pH range from 8 to 11 can be used herein for this purpose, e.g., carbonates, Na_2HPO_4, Na_3PO_4, etc. Especially preferred herein are phosphate buffers, especially ortho-, meta-, and tripolyphosphate salts. While any of the common buffers are useful herein, the phosphate buffer salts have the advantage that they are innocuous when applied to the skin, are efficient buffers over the pH range indicated, and stabilize the peroxide being used by preventing metal ion catalyzed peroxide decomposition. Buffers such as the phosphates can be used at concentrations from about 0.1% to about 5% by weight in the present compositions. When the carbonate and phosphate salts of the guanidine compounds are used herein they act as their own pH buffers and maintain the basicity of the bleaching composition within the optimal range. When such carbonate or phosphate salts are used herein, some additional base or buffer can be included to help maintain pH stability and to help stabilize the peroxygen compound.

Hair bleaching compositions designed for use on the head are difficult to apply properly without the use of thickeners. It is, therefore, desirable to include thickening agents in the herein-disclosed compositions to impart a creamy gel consistency thereto such that they are adapted for localized application. A variety of such thickening agents suitable for use with peroxide hair bleaching compositions are well known in the cosmetic arts and all such thickeners are useful in the present compositions. For example, sodium metasilicate is commonly used for this purpose as are various clays, carboxymethylcellulose compounds and the like. Thickeners can be used at concentrations from about 1% to about 5% of the bleaching compositions.

The present compositions can contain various other adducts to provide a more cosmetically acceptable product. Such materials as perfumes, dyes, and the like can be added to the bleaching compositions detailed herein to provide a more pleasant cosmetic aspect. In addition, trace quantities of stabilizers such as the ethylenediaminetetraacetates, phosphates, citrates and the like may also be used.

HAIR BLEACHING TEST

A hair bleaching test was carried out as follows:

Hair switches were prepared by cutting small amounts from a commercial sample of brown virgin European hair and dipping the cut end in glue. Switches used herein were about six inches long and weighed from 1 to 2 grams. In the bleaching operation the switches were tied to a stirring rod and immersed in 50 ml. of freshly prepared bleaching solution for periods up to 60 minutes. The test compositions were those prepared in Examples I and II below and in Table I. The control bleach comprised 6% by weight hydrogen peroxide containing 6% ammonium peroxydisulfate and about 3% ammonia supplied as 9%

concentrated ammonium hydroxide. Estimates of bleaching activity were made visually by comparing the treated switch to a set of 30 standard switches sequentially number 1–30, with grade 1 being no bleaching and grade 30 being very extensive bleaching, and estimates of bleach damage were made tactilely. The test results indicate that the control system gives a color grade of 16. At the same time, the degree of damage in the three tests (control and first two examples below) were approximately equal, indicating that for a given degree of damage, the barbituric acid compound containing compositions bleach more rapidly than the control bleach.

The following examples serve to illustrate the bleaching compositions of this invention but are not intended to be limiting thereof. In the examples, water is used as the common solvent for the components of the bleach compositions. Water can be replaced, in part, by up to about 50% by liquids such as the lower alcohols, e.g., ethylene glycol, propylene glycol, 1,3-propanediol, ethanol, isopropyl alcohol, glycerine and mixtures thereof. The bleaches herein are applied to hair for periods of one minute to four hours, depending on the degree of bleaching desired. A preferred time is between 20 and 45 minutes.

EXAMPLE I

Ingredient:	Amount, g.
Guanidinium chloride	4.5
Sodium pyrophosphate	2.0
Ammonium peroxydisulfate	3.0
Hydrogen peroxide (30% by weight aqueous solution)	5.0
Barbituric acid	0.5
Water, to 50 ml. total volume.	

The guanidinium chloride, sodium pyrophosphate and ammonium peroxydisulfate were dissolved in about 30 ml. of water, the hydrogen peroxide was added, followed by the barbituric acid and the resulting solution was diluted to 50 ml. The final concentration (wt.) of the bleaching solution of this composition was 3% hydrogen peroxide, 6% ammonium peroxydisulfate, 9% guanidinium chloride, 4% sodium pyrophosphate, and barbituric acid at 1%. The pH of the solution was 9.2. This bleaching composition was successfully used to bleach human hair in the manner detailed in the Hair Bleaching Test, above. A color grade of 22 was obtained.

EXAMPLE II

Ingredient:	Amount, g.
Guanidinium carbonate	4.5
Ammonium peroxydisulfate	3.0
Hydrogen peroxide (30% by weight aqueous solution)	5.0
Barbituric acid	0.5
Water, to 50 ml. total volume.	

The above bleaching composition was prepared by dissolving the guanidinium carbonate and the ammonium peroxy-disulfate in about 30 ml. of water, adding the hydrogen peroxide, followed by the barbituric acid, and diluting the resulting solution to 50 ml. The final concentration in this bleach was 3% hydrogen peroxide, 6% ammonium peroxy-disulfate, 9% guanidinium carbonate, and 1% barbituric acid. The pH was 9.2. The self-buffering bleaching composition prepared in this manner was successfully used to bleach human hair in the Hair Bleaching Test, above. A color grade of 23 was obtained for the above composition.

EXAMPLE III

Ingredient:	Amount, g.
N-methylguanidinium carbonate	4.5
Potassium peroxydisulfate	3.0
Hydrogen peroxide (30% by weight aqueous solution)	5.0
Barbituric acid	0.5
Water, to 50 ml. total volume.	

The above bleaching composition is prepared by dissolving the N-methylguanidinium carbonate and the potassium peroxydisulfate in about 30 ml. of water, adding the hydrogen peroxide, and then the barbituric acid, and diluting the resulting solution to 50 ml. The final concentration in this bleaching solution is 3% hydrogen peroxide, 6% ammonium peroxydisulfate, 9% N-methylguanidinium carbonate, and 1% barbituric acid. The pH of the solution is about 9.2. This self-buffering, non-odorous bleaching composition is applied to human hair and rapidly bleaches it. The pH is adjusted to 8.0 with HCl and equivalent results are secured.

Compositions are prepared in accordance with those prepared in Example III above except that the barbituric acid is replaced by an equivalent amount of:

N-methylbarbituric acid;
N-ethylbarbituric acid;
N-isopropylbarbituric acid;
N-2-methylpentylbarbituric acid;
N,N'-dimethylbarbituric acid;
N,N'-diisopropylbarbituric acid;
N-methyl-N'-isopropylbarbituric acid;
N-isopropyl-N'-hexylbarbituric acid;
N-methyl-N'-hydroxymethylbarbituric acid;
N,N'-bis(hydroxymethyl)barbituric acid;
N,N'-bis(β-hydroxyethyl)barbituric acid;
N-ethyl-N'-6-hydroxyhexylbarbituric acid;
N-methyl-N'-carboxymethylbarbituric acid;
N,N'-bis(carboxymethyl)barbituric acid;
N,N'-bis(carboxypropyl)barbituric acid;
N-propyl-N'-5-carboxypentylbarbituric acid;
N,N'-diphenylbarbituric acid;
N,N'-dinaphthylbarbituric acid;
N,N'-bis(biphenylyl)barbituric acid;
N-phenyl-N'-naphthylbarbituric acid;
N-methyl-N'-phenylbarbituric acid;
N-hydroxyethyl-N'-naphthylbarbituric acid;
N-carboxymethyl-N'-biphenylylbarbituric acid;
N,N'-bis(benzyl)barbituric acid;
N-methyl-N'-benzylbarbituric acid;
N-benzyl-N'-hydroxyethylbarbituric acid;
N-methyl-N'-paraethylphenylbarbituric acid;
N,N'-bis(2-phenylethyl)barbituric acid;

and the sodium potassium and ammonium salts of barbituric acid and the above named compounds, respectively.

In each instance, substantially equivalent results are obtained in that odorless bleaching compositions having shortened bleaching times and less damaging effects on growing hair are obtained.

In the above composition of Example III, the N-methylguanidinium carbonate is replaced by and equivalent amount of N-decylguanidinium carbonate, N-hydroxyethylguanidinium carbonate, N-phenylguanidinium carbonate, N,N'-bis-(hydroxymethyl)guanidinium carbonate, N-phenyl-N-ethylguanidinium carbonate, N,N,N',N'-tetraethylguanidinium carbonate, and N-paramethoxyphenylguanidinium carbonate, respectively, and equivalent results are secured in that the odorless bleaching compositions thereby obtained rapidly bleach growing human hair.

EXAMPLE IV

Thickened bleaching composition

Ingredient:	Percent (wt.)
Guanidinium carbonate	20
Ammonium peroxydisulfate	10
Hydrogen peroxide (30% by weight aqueous solution)	8
Sodium metasilicate	2
Barbituric acid	1
Water	Balance

The above bleaching composition is prepared by dissolving the guanidinium carbonate, the ammonium peroxydisulfate and the hydrogen peroxide in about 50 ml. of

water, adding the barbituric acid, and adding the sodium metasilicate to provide a thickened solution. The bleaching compositions so obtained are essentially odorless and rapidly bleach growing human hair.

Compositions of the type prepared in Example IV are prepared except that the barbituric acid utilized therein is replaced by an equivalent amount of:

N-methylbarbituric acid;
N-ethylbarbituric acid;
N-isopropylbarbituric acid;
N-methyl-N'-isopropylbarbituric acid;
N-isopropyl-N'-hexylbarbituric acid;
N-methyl-N'-hydroxymethylbarbituric acid;
N,N'-bis(hydroxymethyl)barbituric acid;
N,N'-bis(β-hydroxyethyl)barbituric acid;
N-ethyl-N'-6-hydroxyhexylbarbituric acid;
N-methyl-N'-carboxymethylbarbituric acid;
N,N'-bis(carboxymethyl)barbituric acid;
N,N'-bis(carboxypropyl)barbituric acid;
N-propyl-N'-5-carboxypentylbarbituric acid;
N,N'-diphenylbarbituric acid;
N,N'-dinaphthylbarbituric acid;
N,N'-bis(biphenylyl)barbituric acid;
N-phenyl-N'-naphthylbarbituric acid;
N-methyl-N'-phenylbarbituric acid;
N-hydroxyethyl-N'-naphthylbarbituric acid;
N-carboxymethyl-N'-biphenylylbarbituric acid;
N,N'-bis(benzyl)barbituric acid;
N-methyl-N'-benzylbarbituric acid;
N-benzyl-N'-hydroxyethylbarbituric acid;
N-methyl-N'-paraethylphenylbarbituric acid;
N,N'-bis(2-phenylethyl)barbituric acid;

and the sodium, potassium and ammonium salts of barbituric acid and the above named compounds, respectively.

In each instance, the result is a thickened bleaching composition which rapidly and safely bleaches growing human hair.

In the above composition, the guanidinium carbonate is replaced by an equivalent amount of guanidinium phosphate, guanidinium nitrate, guanidinium bicarbonate, N-methyl-quanidinium acetate, and N-phenylquanidinium laurate, respectively. The equivalent hair bleaching compositions so obtained rapidly and safely bleach growing human hair.

In the above composition the ammonium peroxydisulfate is replaced by an equivalent amount of sodium peroxydisulfate, potassium peroxydiphosphate, and potassium peroxydisulfate, respectively, and equivalent bleaching results are secured.

EXAMPLE V

Dry peroxide bleaching composition

Ingredient:	Percent (wt.)
Guanidinium carbonate	40
Sodium perborate	5
Potassium peroxydisulfate	0.5
Ammonium peroxydisulfate	0.5
Sodium metasilicate	2
Sodium tripolyphosphate	2
Barbituric acid	2
Starch	Balance

Ten grams of the above composition is mixed with 50 ml. of water and provides a thickened, buffered bleaching composition which rapidly and safely bleaches growing human hair. The composition is essentially odorless.

In the above composition, each of the following modifications is made:

The sodium perborate is replaced by an equivalent amount of potassium peroxide, potassium percarbonate, and urea peroxide complex, respectively, and the resulting bleach compositions thereby secured are applied to human hair for periods from about 10 minutes to about 2 hours, depending upon the degree of lightness desired, and effectively bleach said hair.

The potassium peroxydisulfate is replaced by an equivalent amount of a 1:1 (wt.) mixture of ammonium peroxydisulfate and ammonium peroxydiphosphate and equivalent bleaching compositions are secured.

The potassium metasilicate is replaced by an equivalent amount of sodium carboxymethylcellulose and a thickened bleach is thereby secured.

The sodium tripolyphosphate is replaced by an equivalent amount of sodium hydrogen phosphate and trisodium phosphate (1:1 wt.) and buffered bleaches are secured.

The sodium perborate is replaced by sodium peroxide at concentrations of 1% and 10% by weight, respectively, and hair bleaching compositions are thereby provided. The sodium perborate in the above compositions is replaced by urea peroxide at concentrations of 1% and 10% by weight, respectively, and odorless hair bleaches are thereby secured.

The guanidinium carbonate is replaced by an equivalent amount of guanidine, N-methylguanidine, N-decylguanidine, N,N,N',N'-tetraphenylguanidine, N,N,N',N'-tetrabutylguanidine, N - hydroxymethylguanidine, N-chlorophenyl-N'-hydroxybutylguanidine and N-phenyl-N-naphthyl-N'-methyl-N'-hydroxymethylguanidine, respectively, and the compositions are buffered at pH 9 with 5% by weight of a sodium hydrogen phosphate-trisodium phosphate buffer and equivalent bleaches are thereby secured.

The barbituric acid of Example V is replaced by an equivalent amount of:

N-methylbarbituric acid;
N-ethylbarbituric acid;
N-isopropylbarbituric acid;
N-2-methylpentylbarbituric acid;
N,N'-dimethylbarbituric acid;
N,N'-diisopropylbarbituric acid;
N-methyl-N'-isopropylbarbituric acid;
N-isopropyl-N'-hexylbarbituric acid;
N-methyl-N'-hydroxymethylbarbituric acid;
N,N'-bis(hydroxymethyl)barbituric acid;
N,N'-bis(β-hydroxyethyl)barbituric acid;
N-ethyl-N'-6-hydroxyhexylbarbituric acid;
N-methyl-N'-carboxymethylbarbituric acid;
N,N'-bis(carboxymethyl)barbituric acid;
N,N'-bis(carboxypropyl)barbituric acid;
N-propyl-N'-5-carboxypentylbarbituric acid;
N,N'-diphenylbarbituric acid;
N,N'-dinaphthylbarbituric acid;
N,N'-bis(biphenylyl)barbituric acid;
N-phenyl-N'-naphthylbarbituric acid;
N-methyl-N'-phenylbarbituric acid;
N-hydroxyethyl-N'-naphthylbarbituric acid;
N-carboxymethyl-N'-biphenylylbarbituric acid;
N,N'-bis(benzyl)barbituric acid;
N-methyl-N'-benzylbarbituric acid;
N-benzyl-N'-hydroxyethylbarbituric acid;
N-methyl-N'-paraethylphenylbarbituric acid;
N,N'-bis(2-phenylethyl)barbituric acid;

and the sodium, potassium and ammonium salts of barbituric acid and the above named compounds, respectively.

In each instance, a bleaching composition having enhanced bleaching properties and safety results.

Additional examples within the scope of the present invention are listed in Table I. In all cases, a 2 g. hair switch was immersed in a 50 ml. test solution as in the "Hair Bleaching Test" above.

TABLE I.—EXAMPLES VI-XI

Example	Percent H_2O_2	$(NH_4)_2S_2O_8$	Guanidinium carbonate	NH_3+	Barbituric acid	Color grade
VI	1	10	9		1	20
VII	3	4	9		1	22
VIII	1	10	9		2	22
IX+	3	6	9			16
X+	3	6		3		14
XI++	6	6		3		16

+Control.
++Control used in Hair Bleaching Test.

In each instance the bleaching compositions of the present invention exhibited superior bleaching characteristics with less hair damage.

Hair bleaching products are typically marketed in kit form, i.e., a package comprising an individually packaged oxidizing component and an individually packaged bleaching assistant. In an embodiment of this invention said oxidizing component consists of a stabilized aqueous solution of a peroxygen compound as detailed herein, most generally aqueous hydrogen peroxide in an amount such that the final concentration of the composition for use on the hair is from about 1% to about 10% by weight, and said bleaching assistant component comprises a barbituric acid compound of the present invention, a bleaching accelerator of the type hereinbefore detailed and a guanidine compound or salt thereof, of the type hereinabove detailed. The components are mixed by the user immediately prior to application to the hair. An example of such kit is as follows:

A hair bleaching kit is assembled comprising a single package including therein: (1) a 4 oz. bottle of hydrogen peroxide (6% by weight H_2O_2); and (2) a foil packet containing a bleaching assistant, said assistant consisting of 4 g. of ammonium peroxydisulfate, 15 g. of guanidinium carbonate; and (3) a 1 oz. bottle containing 2 g. of barbituric acid, 2 g. of sodium carboxymethylcellulose and 10 g. of starch. The bleaching assistant is admixed with the hydrogen peroxide and the contents of the 1 oz. bottle are added thereto. The resulting solution is applied to the hair and bleaches it.

In the above composition the guanidinium carbonate is replaced by an equivalent amount of guanidinium phosphate, guanidinium chloride, N-methylguanidinium phosphate, N-methylguanidinium chloride and N-phenylguanidinium carbonate and equivalent results are secured.

In the above composition the 6% aqueous hydrogen peroxide solution is replaced by an equivalent volume of 3% hydrogen peroxide solution and substantially equivalent results are secured.

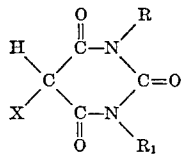
In the above composition the guanidinium carbonate is replaced by 0.1 g. of N-methylguanidinium chloride, 0.5 g. of guanidine, 1.0 g. of N-methylguanidine, 10 g. of N-phenylguanidine, 10 g. of N,N'-diphenylguanidine and 5 g. of N - dodecyl - N' - hydroxymethylguanidinium nitrate, respectively. In each of the respective compositions, 5.0 g. of a buffer consisting of 4.0 g. of Na_2HPO_4 and 1 g. of Na_3PO_4 is included in the bleaching assistant packet. Upon admixture with the peroxide, buffered (pH 9.2) bleaches are secured.

What is claimed is:

1. A hair bleaching composition which is suitable for use in contact with the human skin which comprises:

(A) from about 0.1% to about 10% by weight of a barbituric acid compound having the formula:

(I)



wherein R and R_1 are the same or different and are selected from the group consisting of hydrogen; alkyl groups of from about 1 to about 6 carbon atoms; hydroxyalkyl groups of from about 1 to about 6 carbon atoms; carboxyalkyl groups of from about 1 to about 6 carbon atoms; aryl groups of from about 6 to about 12 carbon atoms; and aralkyl groups of from about 6 to about 14 carbon atoms; and X is selected from the group consisting of hydrogen, sodium, potassium and ammonium;

(B) from about 1% to about 10% by weight of a water-soluble peroxygen compound which yields hydrogen peroxide in solution; and

(C) from about 0% to about 98.9% by weight of an inert diluent, said bleaching composition having a pH of from about 8 to about 11 when used in an aqueous medium.

2. The composition of claim **1** wherein the compound of formula (I) is selected from the group consisting of:

barbituric acid;
N-methylbarbituric acid;
N-ethylbarbituric acid;
N-isopropylbarbituric acid;
N-2-methylpentylbarbituric acid;
N,N'-dimethylbarbituric acid;
N,N'-diisopropylbarbituric acid;
N-methyl-N'-isopropylbarbituric acid;
N-isopropyl-N'-hexylbarbituric acid;
N-methyl-N'-hydroxymethylbarbituric acid;
N,N'-bis(hydroxymethyl)barbituric acid;
N,N'-bis(β-hydroxyethyl)barbituric acid;
N-ethyl-N'-6-hydroxyhexylbarbituric acid;
N-methyl-N'-carboxymethylbarbituric acid;
N,N'-bis(carboxymethyl)barbituric acid;
N,N'-bis(carboxypropyl)barbituric acid;
N-propyl-N'-5-carboxypentylbarbituric acid;
N,N'-diphenylbarbituric acid;
N,N'-dinaphthylbarbituric acid;
N,N'-bis(biphenylyl)barbituric acid;
N-phenyl-N'-naphthylbarbituric acid;
N-methyl-N'-phenylbarbituric acid;
N-hydroxyethyl-N'-naphthylbarbituric acid;
N-carboxymethyl-N'-biphenylylbarbituric acid;
N,N'-bis(benzyl)barbituric acid;
N-methyl-N'-benzylbarbituric acid;
N-benzyl-N'-hydroxyethylbarbituric acid;
N-methyl-N'-paraethylphenylbarbituric acid;
N,N'-bis(2-phenylethyl)barbituric acid;

and the sodium, potassium and ammonium salts of said compounds.

3. The composition of claim **1** wherein the compound of formula (I) is barbituric acid.

4. The composition of claim **1** wherein the water-soluble peroxygen compound is selected from the group consisting of hydrogen peroxide, alkali metal peroxides, sodium perborate, and urea peroxide.

5. The composition of claim **1** which contains from about 0.1% to about 45% by weight of one or more bleach enhancing agents in addition to said barbituric acid compound.

6. The composition of claim **1** which contains, in addition, from about 0.1% to about 45% by weight of one or more bleach enhancing agents selected from the group consisting of a guanidine compound selected from the group consisting of guanidinium carbonate, guanidinium chloride, and guanidinium phosphate; ammonium hydroxide, ammonium peroxydisulfate, potassium peroxydisulfate, sodium peroxydisulfate and potassium peroxydiphosphate.

7. The composition of claim **1** which contains, in addition, from about 0.1% to about 5% by weight of a peroxygen-compatible buffer capable of maintaining a pH of from about 8 to about 11 in aqueous solution.

8. A hair bleaching composition according to claim 1 which comprises:

(A) from about 0.8% to about 3% by weight of said barbituric acid compound;

(B) from about 2% to about 6% by weight of a water-soluble peroxygen compound selected from the group consisting of hydrogen peroxide, sodium perborate, and urea peroxide;

and which contains in addition:

(C) from about 3% to about 8% by weight of a bleach enhancing agent selected from the group consisting of ammonium peroxydisulfate, potassium peroxydisulfate, sodium peroxydisulfate, potassium peroxydiphosphate, and mixtures thereof;

(D) from about 2% to about 10% by weight of a bleach enhancing agent selected from the group consisting of guanidinium carbonate, guanidinium chloride, guanidinium phosphate, and mixtures thereof; and

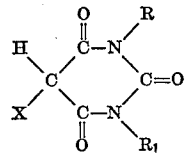
(E) balance, water.

9. The composition of claim 8 which contains, in addition, from about 0.1% to about 5% by weight of a peroxygen-compatible buffer capable of maintaining a pH of from about 8 to about 11 in aqueous solution.

10. A process for bleaching hair which comprises applying to the hair an effective amount of an aqueous hair bleaching composition which is suitable for use in contact with the human skin and which comprises:

(A) from about 0.1% to about 10% by weight of a barbituric acid compound having the formula:

(I)



wherein R and R_1 are the same or different and are selected from the group consisting of hydrogen; alkyl groups of from about 1 to about 6 carbon atoms; hydroxyalkyl groups of from about 1 to about 6 carbon atoms; carboxyalkyl groups of from about 1 to about 6 carbon atoms; aryl groups of from about 6 to about 12 carbon atoms; and aralkyl groups of from about 6 to about 14 carbon atoms; and X is selected from the group consisting of hydrogen, sodium, and potassium ammonium;

(B) from about 1% to about 10% by weight of a water-soluble peroxygen compound which yields hydrogen peroxide in solution; and

(C) from about 0% to about 98.9% by weight of an inert diluent, said bleaching composition having a pH of from about 8 to about 11.

11. The process according to claim 10 for bleaching hair wherein the compound having formula (I) is selected from the group consisting of:

barbituric acid;
N-methylbarbituric acid;
N-ethylbarbituric acid;
N-isopropylbarbituric acid;
N-2-methylpentylbarbituric acid;
N,N'-dimethylbarbituric acid;
N,N'-diisopropylbarbituric acid;
N-methyl-N'-isopropylbarbituric acid;
N-isopropyl-N'-hexylbarbituric acid;
N-methyl-N'-hydroxymethylbarbituric acid;
N,N'-bis(hydroxymethyl)barbituric acid;
N,N'-bis(β-hydroxyethyl)barbituric acid;
N-ethyl-N'-6-hydroxyhexylbarbituric acid;
N-methyl-N'-carboxymethylbarbituric acid;
N,N'-bis(carboxymethyl)barbituric acid;
N,N'-bis(carboxypropyl)barbituric acid;
N-propyl-N'-5-carboxypentylbarbituric acid;
N,N'-diphenylbarbituric acid;
N,N'-dinaphthylbarbituric acid;
N,N'-bis(biphenylyl)barbituric acid;
N-phenyl-N'-naphthylbarbituric acid;
N-methyl-N'-phenylbarbituric acid;
N-hydroxyethyl-N'-naphthylbarbituric acid;
N-carboxymethyl-N'-biphenylylbarbituric acid;
N,N'-bis(benzyl)barbituric acid;
N-methyl-N'-benzylbarbituric acid;
N-benzyl-N'-hydroxyethylbarbituric acid;
N-methyl-N'-paraethylphenylbarbituric acid;
N,N'-bis(2-phenylethyl)barbituric acid;

and the sodium, potassium and ammonium salts of said compounds.

12. A process according to claim 10 wherein the compound of formula (I) is present in an amount of from about 0.8% to about 3% by weight and is barbituric acid.

13. A process according to claim 10 wherein the water-soluble peroxygen compound is present in an amount of from about 2% to about 6% by weight and is selected from the group consisting of hydrogen peroxide, alkali metal peroxides, sodium perborate, and urea peroxide.

14. A process according to claim 10 wherein the bleaching composition contains from about 0.1% to about 45% of one or more bleach enhancing agents in addition to said barbituric acid compound.

15. A process according to claim 10 wherein the bleaching composition contains, in addition, a bleach enhancing agent selected from the group consisting of a guanidine compound selected from the group consisting of guanidinium carbonate, guanidinium chloride, and guanidinium posphate; ammonium hydroxide, ammonium peroxydisulfate, potassium peroxydisulfate, sodium peroxydisulfate, potassium peroxydiphosphate, and mixtures thereof.

16. A process according to claim 10 wherein the bleaching composition contains, in addition, from about 0.1% to about 5% by weight of a peroxygen-compatible buffer capable of maintaining a pH of from about 8 to about 11 in aqueous solution.

17. The composition of claim 1 which contains, in addition, from about 0.1% to about 45% by weight of an additional bleach enhancing agent selected from the group consisting of ammonium hydroxide, alkali metal peroxydisulfate, ammonium peroxydiphosphate, alkali metal peroxydiphosphate, guanidine, and a soluble guanidinium salt.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,816,614 Dated June 11, 1974

Inventor(s) Eugene Zeffren & Richard B. Knohl

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 13, line 47, "and potassium ammonium" should read --- potassium and ammonium ---.

Col. 14, line 39, "posphate" should read --- phosphate ---.

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

[redacted]

PO-1050
(5/69)

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