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[54] Title: STABILIZED PARTICULATE HYDROGEN PEROXIDE ADDUCTS AND THEIR USE

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[57] ABSTRACT

Particulate hydrogen peroxide adducts are coated with water-soluble homopolymers or copolymers bearing free carboxyl groups, preferably of acrylic or methacrylic acid, in the acid form. Stability in storage is thus increased without any problems arising in regard to the evolution of hydrogen peroxide on contact with water. An aqueous solution of the polymer is preferably sprayed on in a fluidized bed and the water is removed by drying.

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Stabilized particulate hydrogen peroxide adducts and their use

Particulate hydrogen peroxide adducts are coated with water-soluble homopolymers or copolymers bearing free carboxyl groups, preferably of acrylic or methacrylic acid, in the acid form. Stability in storage is thus increased without any problems arising in regard to the evolution of hydrogen peroxide on contact with water. An aqueous solution of the polymer is preferably sprayed on in a fluidized bed and the water is removed by drying.

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BUREAU OF PATENTS, TRADEMARKS AND TECHNOLOGY TRANSFER

Patent Application
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Stabilized particulate hydrogen peroxide adducts and their use

This invention relates to stabilized, particulate hydrogen peroxide adducts, to a process for their production by coating with water-soluble polymers containing carboxyl groups in the acid form and to their use as oxidant component in powder-form oxidation hair dyes.

Particulate hydrogen peroxide adducts are used for numerous bleaching and oxidation processes, particularly in powder-form preparations in which they are often present together with other components, for example surfactants, dyes, optical brighteners, perfumes, antimicrobial agents and other substances sensitive to oxidation. A particular problem in this regard is the stability of the hydrogen peroxide adduct which readily decomposes with evolution of oxygen, particularly under the effect of moisture, and damages the other oxidation-sensitive components of the preparations.

Accordingly, there has been no shortage of attempts to protect particulate hydrogen peroxide adducts against premature decomposition by additives, granulation aids or even by coating with various substances.

DE 24 02 392 C2 for example describes a process for stabilizing sodium percarbonate particles by coating with a copolymer of vinylidene chloride and another polymerizable monomer, for example of vinyl chloride, acrylonitrile or an acrylate or methacrylate.

Particles of hydrogen peroxide adducts such as these

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coated with water-insoluble polymers have the disadvantage, particularly when used as a component of powder-form hair dyes, that they do not release the hydrogen peroxide quickly enough when the dye is mixed with water and, accordingly, cause a delayed and unsatisfactory evolution of the oxidation dye, resulting in changes of shade and in uneven hair coloration.

It was known from other publications, for example Norda Briefs No. 445, December 1972, that certain hydrogen peroxide adducts, for example trisodium citrate diperhydrate, can be stabilized by coating with fatty acid, wax, paraffin, polyvinyl alcohol or cellulose esters. Although the adducts obtained in this way show somewhat improved stability in storage, the effect of the water-insoluble coating materials is unsuitable for use in powder-form oxidation hair dyes for the reasons explained above. Water-soluble, polymeric coating materials, for example polyvinyl alcohol, are attended by the problem of inadequate stability to moisture, particularly where basic components are present in the preparation.

DE 36 36 904 describes a process for coating per acid granulates. However, the peroxycarboxylic acids described therein are not suitable as oxidant component for oxidation hair dyes because they destroy the oxidation dye.

DE 34 34 468 describes a process for the production of powder-form, free-flowing hydrogen peroxide adducts in which the powder-form hydrogen peroxide adducts are dry-mixed with a polyalkylene glycol, for example polyethylene glycol having an average molecular weight of 200 to 400, in a quantity of 0.5 to 5.0% by weight. Although the particles of the adduct are also coated in this way, the products still tend to become tacky on contact with atmospheric moisture and tend to become unstable in powders containing alkaline components.

Accordingly, the object of the present invention is more effectively to stabilize particulate hydrogen peroxide adducts against decomposition and against attack by atmospheric moisture and to provide stabilized particulate adducts which are more suitable than the known products as components for the production of powder-form oxidation hair dyes.

The present invention relates to stabilized, particulate hydrogen peroxide adducts which are coated with water-soluble polymers and of which the coating consists of a water-soluble homopolymer or copolymer bearing free carboxyl groups. In the context of the invention, free carboxyl groups are those which are present in the acid form (-COOH) and not in neutralized salt form.

Suitable hydrogen peroxide adducts or "peroxide adducts" are the known solid adducts of hydrogen peroxide with inorganic or organic molecules such as, for example, sodium perborate monohydrate ($NaBO_2 \cdot H_2O_2$), sodium perborate tetrahydrate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$), perborax ($Na_2B_4O_7 \cdot 4H_2O_2$), peroxypyrophosphates, citrate perhydrate (for example according to DE 19 20 831), amino-1,3,5-triazine perhydrate (melamine perhydrate according to DE 11 03 934), urea perhydrate (percarbamide according to US 3,629,331), sodium percarbonate ($Na_2CO_2 \cdot H_2O_2$). Particularly suitable particulate adducts are those which have a particle size distribution in which more than 90% of the particles are from 0.1 to 1.0 mm in diameter and less than 1% are larger than 1.0 mm in diameter.

Suitable water-soluble polymers bearing free carboxyl groups are any homopolymers and copolymers of unsaturated carboxylic acids, for example acrylic acid, methacrylic acid, crotonic acid, α-hydroxyacrylic acid, maleic acid, alkyl acetic acid, 2-alkyloxypropionic acid, 2-vinyl propionic acid or vinyl acetic acid.

Suitable comonomers are, for example, styrene, acrylates or methacrylates, acrylamide, methacrylamide, diesters of maleic and fumaric acid, vinyl esters and vinyl ethers, although no more than up to 20 mol-% of these water-insoluble comonomers should be used.

The homopolymers and copolymers of acrylic or methacrylic acid are particularly suitable. In one preferred embodiment, the coating material consists of a polyacrylic acid having a specific viscosity in the range from 0.07 to 0.9 and preferably in the range from 0.10 to 0.20. The specific viscosity (v spec.) is understood to be the quotient $(v - v_0) / v_0$, where v is the viscosity of a solution of the sodium salt and v_0 is the viscosity of the solvent. In the present case, the viscosity of a 0.7% solution of the Na salt (% by weight) in a 2 N sodium hydroxide was measured.

The coating material preferably makes up from 2 to 20% by weight of the coated hydrogen peroxide adduct.

In the most simple case, the particulate hydrogen peroxide adducts stabilized in accordance with the invention may be produced by spraying an aqueous solution of the homopolymer or copolymer bearing free carboxyl groups onto the particulate hydrogen peroxide adducts and removing the water simultaneously and, optionally, also subsequently by drying. In this way, the particles of the hydrogen peroxide adducts are coated with the polymer.

Numerous types of apparatus suitable for drying powder-form solids may be used to carry out this coating process.

In order to prevent sticking of the particles and coarsening thereof by granulation processes during the coating process, it is of advantage continuously to move the particles during drying with a stream of heated air.

One preferred embodiment of the process according to the invention is characterized in that the aqueous solution of the homopolymer or copolymer is sprayed on and the particulate hydrogen peroxide adduct is dried in a fluidized bed into which a stream of heated air or inert gas is introduced. Nitrogen for example may be used as the inert gas. In the fluidized bed coater particularly suitable for this process, the air or inert gas stream is introduced through a sieve plate on which the particulate material is situated. The particulate material is converted by the air or inert gas stream into a fluidized bed in which the individual particles are in constant motion. The temperature of the air or inert gas stream is high enough to heat the fluidized particulate material to around 35 - 50°C.

After the coated, particulate hydrogen peroxide has been dried, it is cooled to a temperature below 35°C by the introduction of a cold air stream.

In one preferred embodiment of the process according to the invention, the homopolymer or copolymer is sprayed in the form of a 5 to 30% by weight aqueous solution and in a quantity of 2 to 20 parts by weight onto 80 to 98 parts by weight of the hydrogen peroxide adduct.

The particulate hydrogen peroxide adducts coated in accordance with the invention and thus stabilized show high stability in storage, even at elevated temperatures, for example of up to +50°C. They are suitable as oxidant for powder-form preparations for numerous bleaching and oxidation processes.

The particulate hydrogen peroxide adducts according to the invention are particularly suitable as oxidant component in powder-form oxidation hair dyes.

Oxidation hair dye powders, as known for example from DE 11 41 749 or from DE 11 77 775, consist of a powder-form mixture of oxidation dye precursors, powder-form water-soluble thickeners and, optionally, powder-form extenders, surfactants, stabilizers and a particulate hydrogen peroxide adduct as oxidant component.

The particulate hydrogen peroxide adducts stabilized in accordance with the invention have the following technical advantages in compositions such as these: the viscosity of the dye preparations obtained from the oxidation hair dye powders by mixing in water remains largely unchanged, even after prolonged storage of the powder, because the oxidant component is effectively prevented from attacking the polymeric thickener. The content of active oxygen remains constant over prolonged periods of storage. The dye preparations obtained by mixing of the oxidation hair dye powders with water show greater smoothness and uniformity because the swelling of the powder-form, water-soluble thickeners is favorably influenced.

The powder-form oxidation hair dyes prepared with the particulate hydrogen peroxide adducts stabilized in accordance with the invention preferably have the following composition:

0.04 - 0.4 mol/100 g oxidation dye precursors,
1 to 20% by weight of an anhydrous zeolite drying agent,
10 to 30% by weight of a water-soluble polymeric thickener,
10 to 40% by weight of a particulate hydrogen peroxide adduct stabilized in accordance with the invention,
2 to 20% by weight of a powder-form, water-soluble surfactant.

Developers and, optionally, couplers are used as the oxidation dye precursors.

The developer components form the actual dyes under the influence of the oxidant or atmospheric oxygen either on their own or by coupling with one or more coupler components.

The developer components normally used are primary, aromatic amines containing another free or substituted hydroxy or amino group in the para position or ortho position or salts thereof; diaminopyridine derivatives, heterocyclic hydrazone derivatives, 4-aminopyrazolone derivatives and 2,4,5,6-tetraaminopyridine and derivatives thereof. Particularly important developer components are p-phenylenediamine, p-tolylenediamine, p-aminophenol and 2,4,5,6-tetraaminopyridimine.

Coupler compounds are used to modify the shades and to increase brilliance and fastness. Suitable coupler components are, for example, m-phenylenediamines, m-aminophenols or salts thereof, m-dihydroxybenzene, 1-naphthol, 1,5- and 2,7-dihydroxynaphthalene, hydroxy and aminopyridines, hydroxyquinolines and aminopyrazolones. Particularly important coupler components are m-phenylenediamine, 3-aminophenol and m-dihydroxybenzene and derivatives thereof. The developer and coupler components are generally used in equimolar quantities, although a certain excess of individual oxidation dye precursors is not harmful so that the developer components and coupler components may be used in a molar ratio of 1 : 0.5 to 1 : 2. The developer components are preferably used in the oxidation hair dye powders in a quantity of 0.02 to 0.2 mol/100 g while the coupler components are preferably used in a quantity of 0.01 to 0.2 mol/100 g.

The zeolite drying agent is preferably a synthetic, completely or substantially anhydrous crystalline alkali aluminium silicate of zeolite structure which generally contains no more than 3% and preferably no more than 1.5% water and, accordingly, has a high moisture absorption capacity. Particularly suitable zeolites are the synthetic zeolites of type A and/or X in powder form. Products such as these are commercially available, for example as Baylith (R)-L-Pulver (Bayer AG), a zeolite of the NaA type with an apparent density of 400 to 450 g/dm^3; or the products "Molekularsiebe UETIKON Puder" of Chem. Fabr. UETIKON (Switzerland), of which the sodium forms of zeolites A and X are again preferably used. However, the zeolites mentioned may also be used in granulated form, i.e. as agglomerates between about 1 and 2 mm in diameter, which may be used as binder-containing or binder-free products. Dried amorphous sodium aluminium silicates in powder form or in granulated form may also be used in accordance with the invention, albeit with a weaker stabilizing effect, acting as drying agents even with a water content higher than 3%; they are also regarded as zeolite drying agents in the context of the invention.

After stirring with water, the oxidation hair dye powders should give a creamy or gel-like dye preparation. This requires the presence of a water-soluble thickener. Suitable water-soluble thickeners are natural and synthetic polymers in powder or finely divided, free-flowing form which dissolve in water with a considerable increase in viscosity. Examples of such polymers are water-soluble derivatives of cellulose, for example carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose, alginates, starch derivatives and other water-soluble polysaccharides such as, for example, guar gum, water-soluble guar derivatives and xanthan gum. It is also possible to use synthetic polymers such as, for example, polyacrylamides and copolymers of acrylic acid, methacrylic acid or crotonic acid with vinyl compounds.

Sodium alginate is preferably used as the water-soluble thickener. It is preferably used in a quantity of from 10 to 30% by weight.

To make the dissolving process easier and to produce a uniform hair coloration, the oxidation hair dye powders contain one or more finely divided or powder-form water-soluble surfactants.

Particularly suitable surfactants of this type are the alkali salts of sulfuric acid semiesters of linear or slightly branched C_{10-16} fatty alcohols, for example sodium lauryl sulfate. Other suitable powder-form anionic surfactants are, for example, the alkali salts of linear and branched-chain alkyl benzenesulfonates containing 6 to 16 carbon atoms in the alkyl group, alkene and hydroxyalkane sulfonates of the type obtained by sulfonation of C_{10-18} α-olefins, sulfosuccinic acid monoalkyl ester alkali salts containing 8 to 18 carbon atoms in the alkyl group, sulfosuccinic acid dialkyl ester alkali salts containing 6 to 10 carbon atoms in the alkyl group, mono- and dialkyl naphthalenesulfonate alkali salts containing 1 to 8 carbon atoms in the alkyl group, alkyl polyglycol ether carboxylates containing 8 to 18 carbon atoms in the alkyl group and 2 to 6 glycol ether groups in the molecule, acyl sarcosines, acyl taurides and acyl isethionates containing 8 to 18 carbon atoms in the acyl group and α-sulfofatty acid methyl ester alkali salts of C_{8-18} fatty acids.

It is also possible to use solid, fine-grained preparations of surface-active agents which, in pure form, cannot be converted into free-flowing powders and inert auxiliaries and carriers which provide for a non-tacky, fine-grained, free-flowing formulation of these surfactants which are paste-like, low-melting or tacky in pure form. Suitable auxiliaries and carriers of the type in question are preferably readily soluble in water. Water-soluble auxiliaries and carriers are, for example, inorganic, water-soluble salts such as, for example, sodium sulfate, sodium chloride, sodium carbonate, sodium hydrogen carbonate, sodium phosphate and, optionally, the corresponding potassium or ammonium salts. Other non-salt-like water-soluble carriers, such as for example urea or water-soluble mono- and disaccharides, may also be used.

In addition, the oxidation hair dye powders may contain other auxiliaries in small quantities, for example in quantities of from 0.5 to 5% by weight, including for example substantive dyes, perfumes, complexing agents, sodium sulfite, finely divided silica or pigments. They may also contain hair-cosmetic auxiliaries for improving the cosmetic properties of the hair. Of the auxiliaries in question, particular significance is attributed to the cationic water-soluble polymers because they provide the hair with good combability and body and improve its style-holding properties.

Other hair-cosmetic auxiliaries which are advantageously added to improve the combability and to reduce the static charging of hair are cationic surface-active agents of the quaternary ammonium compound type. Surface-active agents of this type are preferably compounds which contain a quaternary ammonium group in the form of the chloride, bromide, sulfate, phosphate, methosulfate or ethosulfate which is substituted by one or two long-chain, preferably linear, alkyl, hydroxyalkyl or alkyl (poly)oxyethyl groups containing 10 to 22 carbon atoms in the alkyl or hydroxyalkyl group and by one or two alkyl-, hydroxyalkyl or polyhydroxyalkyl groups containing 1 to 4 carbon atoms in the alkyl group and, optionally, by a benzyl group. Alkyl pyridinium salts and alkyl imidazolinium salts containing 10 to 22 carbon atoms in the alkyl group are also suitable. Quaternary ammonium compounds such as these are preferably added to the oxidation hair dye powders according to the invention in a quantity of 0.1 to 10% by weight. Examples of suitable quaternary ammonium compounds are cetyl trimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride, stearyl-tris-(polyoxyethyl)-ammonium phosphate, cetyl pyridinium chloride, distearyl dimethyl ammonium chloride or 2-hydroxyhexadecyl-2-hydroxyethyl dimethyl ammonium chloride.

The oxidation hair dye powders are prepared by mixing of the components.

The oxidation hair dyes are readily applied by mixing 1 part by weight of the powder with 5 to 15 parts by weight water. A creamy to gel-form dye preparation having a pH value of from about 6 to 9 is formed. It may be applied to the hair, for example with a brush. After a contact time of about 5 to 30 minutes, the excess dye is rinsed out from the hair.

The following Examples are intended to illustrate the invention without limiting it in any way.

EXAMPLES

1. Coating of sodium perborate monohydrate ($NaBO_2 \cdot H_2O_2$) with polyacrylic acid

1.1 950 g sodium perborate monohydrate (1) were introduced into a fluidized bed coater of the "Uniglatt" type (manufacturer: GLATT). The powder was fluidized by an airstream preheated to around 100°C of which the flow rate through the sieve plate of the coater was approximately 1 to 1.2 m/s. 263 g of a 20% by weight aqueous solution of a polyacrylic acid (2) were applied to the fluidized material through a 1.2 mm two-component nozzle operated with 3 bar compressed air. A constant temperature of approximately 47°C was established in the fluidized bed for a spraying rate of 18 g/minute. After spraying, the product (3) was cooled to a temperature below 35°C by fluidization with cold air.

The following raw materials were used:

(1) Sodium perborate monohydrate ($NaBO_2 \cdot H_2O_2$)

active oxygen content:		15.3% by weight
apparent density:		590 kg/m^3
particle size	above 0.8 mm	0.1% by weight
distribution:	above 0.1 mm	99.9% by weight

appearance: white, crystalline free-flowing substance

(2) Polyacrylic acid

appearance: fine white powder

specific viscosity: 0.15

(0.7% by weight in 2N NaOH solution)

pH value (20% by weight in water): 2.0

The coated sodium perborate monohydrate (3) had the following characteristic data:

apparent density:		610 g/l
particle size distribution		
(screen analysis):	above 0.8 mm	0.7% by weight
	above 0.1 mm	99.8% by weight
active oxygen content:		14.5% by weight
proportion by weight coating material:		5.2% by weight

1.2 In a second experiment, approx. 556 g of a 20% by weight aqueous solution of polyacrylic acid (2) was applied to 890 g sodium perborate monohydrate (1) under otherwise the same conditions as in 1.1. The coated product (4) obtained had the following characteristic data:

apparent density:		630 g/l
particle size distribution		
(screen analysis):	above 0.8 mm	0.6% by weight
	above 0.1 mm	99.9% by weight
active oxygen content:		13.6% by weight
proportion by weight coating material:		11.1% by weight

2. Production of an oxidation hair dye powder

The following composition was prepared by mixing of the components:

	% by weight
p-Phenylenediamine	21.0
p-Aminophenol	1.0
Na aluminium silicate (Baylith L)[1]	8.0
Na alginate	17.0
Hydroxyethyl cellulose	9.0
Na perborate monohydrate from Example 1.1	30.0

	% by weight
Na laurylsulfate	10.0
Silica (Aerosil 200)	1.0
Cationic cellulose derivative (Polymer IR 400, Union Carbide)	1.0
Na_2SO_3	2.0

After addition of 9 parts by weight water to 1 part by weight of the composition, the product gives a ready-to-use dye preparation for producing a deep brown hair coloration.

After storage for 24 hours at 35°C, 45°, 50°C and 60°C, the composition showed no change in viscosity of the dye preparations produced therewith.

If oxidation hair dye powders of the same composition, but without an Na perborate monohydrate stabilized in accordance with the invention, are stored for 24 hours at elevated temperature, the dye preparations produced therewith show greatly increased viscosity values, for example an increase in viscosity of 150% after storage for 24 hours at 50°C.

CLAIMS:

1. Stabilized, particulate hydrogen peroxide adducts coated with water soluble polymers, characterised in that the coating material consists of a water-soluble homopolymer or copolymer of acrylic or methacrylic acid in the acid form, having a specific viscosity of from 0.1 to 0.2 in a quantity of 2 to 20% by weight of the product as a whole.

2. Stabilized, particulate hydrogen peroxide adducts as claimed in Claim 1, characterized in that the hydrogen peroxide adduct consists of sodium perborate monohydrate.

3. A process for the production of the stabilized coated particulate hydrogen peroxide adducts claimed in Claim 1, characterised in that an aqueous solution of the homopolymer or copolymer of acrylic or methacrylic acid is sprayed onto the particulate hydrogen peroxide adducts and the water is removed by drying in a fluidized bed into which a heated stream of air or an inert gas is introduced.

4. A process as claimed in Claim 3, characterized in that 2 to 20 parts by weight of the homopolymer or copolymer in the form of a 5 to 30% by weight aqueous solution are sprayed onto 80 to 98 parts by weight of the hydrogen peroxide adduct.

5. A powdered solid oxidative hair dye preparation, suitable for mixing with water to form a hair dye, comprising as its oxidant component the stabilized, particulate hydrogen peroxide adducts as claimed in Claim 1.

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