

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 585 038 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**26.07.2000 Bulletin 2000/30**

(51) Int. Cl.<sup>7</sup>: **C11D 3/08**, C11D 3/39,  
D06L 3/02, C11D 7/14

(21) Application number: **93306496.6**

(22) Date of filing: **18.08.1993**

(54) **Alkali containing silica solution**

Basische Silikatlösung  
Solution alcaline de silica

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE**

• **Owen, Charlotte Ruth**  
**Wirral, Merseyside L62 5EJ (GB)**

(30) Priority: **28.08.1992 EP 92307886**

(74) Representative:  
**Jackson, John Derek et al**  
**Crosfield Limited**  
**Warrington Cheshire WA5 1AB (GB)**

(43) Date of publication of application:  
**02.03.1994 Bulletin 1994/09**

(73) Proprietor: **CROSFIELD LIMITED**  
**Warrington, Cheshire WA5 1AB (GB)**

(56) References cited:  
**EP-A- 0 210 952**                      **EP-A- 0 407 626**  
**DE-A- 2 147 300**                      **FR-A- 2 643 093**  
**GB-A- 923 897**                        **GB-A- 1 123 071**  
**US-A- 2 838 459**                      **US-A- 3 150 918**  
**US-A- 3 449 254**

(72) Inventors:  
• **Aldcroft, Derek**  
**South Wirral, Cheshire L66 2YZ (GB)**

**EP 0 585 038 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description****Field of the Invention**

5 [0001] The invention relates to alkali containing silica solution containing organic calcium sequestrant, to a bleaching bath formulation containing said silica solution and to a process for the alkaline hydrogen peroxide bleaching of textiles.

**Background of the Invention**

10 [0002] Silicates are well characterised in the literature, for example "The Chemistry of Silica" by R.K. Iler (published by Wiley Interscience 1979) and they have many forms depending on the cation associated with the silicate species, the ratio of metal oxide of this cation to the silicon dioxide content of the solution, and the total solids content. Silicate liquors find uses as sealants adhesives, protective coatings, binders and also stabilisation system in the hydrogen peroxide bleaching of textiles, for example cotton and polyester/cotton (see "The Encyclopedia of organic Chemistry", Kirk Othmer, 3rd Edition, Supplement Vol.3, 1979, pages 877 and 949).

15 [0003] Whilst silicate containing either potassium or sodium oxide, usually referred to as potassium or sodium silicate, is recognised as being the best stabilising system for alkaline hydrogen peroxide bleaching of cotton and polyester/cotton (white goods), i.e. the reaction of the soluble silicate to prolong the active life of the hydrogen peroxide in the bleaching bath, the drawbacks of using silicate are well documented.

20 [0004] Usually, in a textile mill that continuously bleaches white goods with alkaline hydrogen peroxide in a single stage operation where sodium silicate is used as a bleach stabiliser, the following problems manifest:

- Silicate based deposits scale the preparation machinery giving rise to distortion of the fabric and preventing smooth running of the fabric through the equipment;
- Silicate scale builds inside heat exchangers and lowers the effectiveness of preheating the incoming water supply;
- Silicate based residues deposit on the white goods being bleached resulting in harshness, "handle", on the bleached material, high frictional properties on the yarns and fibres yielding poor sewability and faulty dye spotting;
- Poor rinsability requiring large volumes of water to remove these residues from the fabrics.

30 [0005] As a consequence, the textile mill choosing the use of sodium silicate to stabilise an alkaline hydrogen peroxide bleaching process would dose conditioning chemicals to the bleaching bath to minimise these detrimental effects but adding to the complexity of the operation.

35 [0006] Commonly used conditioning chemicals are organic acid calcium sequestrants, fibre conditioning agents and anti-redeposition aids. Including the bleaching system, this can mean up to six streams of chemicals which need to be carefully metered to the bleaching bath, all of which having different reactivities, pH and concentrations.

40 [0007] Moreover, these chemicals can readily react with each other neutralising their conditioning action. This propensity to interact will increase if the mixing is poor and, in a bleaching bath, the only disturbance is the ribbon of cloth moving through the treatment zone. Thus, the textile mill uses higher concentrations of the conditioning chemicals, particularly organic acid sequestrants. In addition, the poor mixing regime in the bleaching bath can result in the silicate solution being destabilised by the acid stream of hydrogen peroxide.

45 [0008] Simplifying the complexity of the alkaline hydrogen peroxide bleaching process gives the Textile Mill added commercial advantages in the reduction of inventory control i.e. less chemicals to purchase and store, and also eliminates the need for expensive metering equipment to ensure accurate dosing of the organic acid calcium sequestrants to the bleaching bath.

**Prior Art**

50 [0009] The use of sodium silicate having a  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio of 1.0 to 2.5 in combination with a magnesium salt and an alkaline metal phosphate for stabilising peroxide solutions suitable for bleaching cotton fabrics is disclosed in US-A-2,838, 459 (Pennalt Chemicals Corp.). In US-A-3,391,594, (Pennalt Chemicals Corp.) the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of the silicate solution is extended below 1.0 to the orthosilicate, but again the presence of magnesium salt, in this case magnesium polyphosphate, is considered to be essential to attain the necessary bleaching effectiveness.

55 [0010] The metal oxide associated with the silicate is usually  $\text{Na}_2\text{O}$ . However, in US-A-4,337,060 (Villar Inc.) it is disclosed potassium silicates can also be used and indeed benefits such as improved cloth handle and elimination of deposits are described. US-A-4,384,970 (L'Air Liquide) teaches improved performance in the stabilisation of peroxide bleaching systems by the use of colloidal magnesium silicate in conjunction with diethylenetriamine penta acetic acid (D.T.P.A.) and diethylenetriamine penta methylene phosphonic acid (D.T.P.M.P.).

**[0011]** Other organic acids and calcium sequestrants including poly-alpha-hydroxy acid or alkoxy-acrylic acid, homopolymer of (meth)acrylic acid or copolymer of acrylic acid with methacrylic acid, (meth)acrylamide, (meth)acrylonitrile, (meth)acrylate esters or other ethylenically unsaturated mono or di-carboxylic acid, and/or copolymer of maleic acid with styrene are described in DE-A-3,423,452(Sandoz) as benefiting the alkaline hydrogen peroxide bleaching process. More particularly, it is disclosed that those organic acids avoid the use of alkaline silicates as stabilisers.

**[0012]** DE-A-2147300 discloses liquid cleansing compositions which exhibit the stable properties of a homogeneous, single phase aqueous liquid and which comprise an aqueous mixture of from 21 to 28% by weight of sodium silicate in which the weight ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  is within the range of 0.5:1 to 1:1 and from 4 to 7% by weight of trisodium or tripotassium nitriloacetate.

**[0013]** EP-A-0407626 discloses a liquid washing and cleaning product containing (A) 5 to 60% by weight potassium carbonate, (B) 1 to 40% by weight alkali silicate with a  $\text{M}_2:\text{SiO}_2$  molar ratio of 1:2 to 1:4 (where M represents sodium or potassium), (C) 1 to 30% by weight of an organic builder such as the sodium or potassium salts of nitriloacetic acid or 1-hydroxy-1,1-diphosphonic acid, (D) 1 to 20% by weight of a polymeric complexing agent and (E) 30 to 80% by weight water (constituents (A) to (D) being calculated on as anhydrous substances).

**[0014]** FR-A-2643093 discloses improved bleaching of cellulosic fibres under alkaline conditions using a peroxide in the presence of an alkali metal silicate, the bleaching bath also containing an amino-polyphosphonic acid but devoid of alkaline earth ions. The bleaching formulations consists of in wt.% (based on the wt. of solid material) 1-15% of alkali metal silicate, 2-30% of amino-polyphosphonic acid, 10-15% of NaOH or KOH and water to make up to 100%.

**[0015]** EP-A-0210952 discloses the bleaching of cellulose-containing fibrous material using an aqueous composition containing (a) an aminopoly(alkylene phosphonic acid), an alkanepolyphosphonic acid and/or an alkali metal salt of a polyaminocarboxylic acid, (b) a poly-OH compound, (c) an alkali metal silicate, (d) an alkali metal hydroxide, (e) a Mg salt, and (f) an alkali metal salt of an alkyl-, aryl- or alkaryl disulphonic acid as anionic dispersant.

**[0016]** It has now been found that, within a selected  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio and concentration range, alkaline containing silica solutions can be made compatible with the neutralised form of organic acid calcium sequestrants. It has been demonstrated that these alkaline containing silica solutions can be used in the alkaline hydrogen peroxide bleaching of white goods, giving equivalent or better whiteness than that obtained with a normal silicate solution, with similar hydrogen peroxide consumption, and none of the detrimental effects usually associated with silicate. These are other benefits resulting from the use of the modified silicate as a stabiliser in the alkaline hydrogen peroxide bleaching of white goods. These are concerned with reducing the complexity of controlling the bleaching bath. For example, the addition of sodium hydroxide can be significantly reduced, if not eliminated in some cases, and there is no need to dose separately an organic acid calcium sequestrant to the bleaching bath.

### General Description of the Invention

**[0017]** According to a first aspect of the invention there is provided an alkali containing silica solution comprising 15 to 30% by weight of silica, 10 to 25% by weight of sodium oxide, 2 to 6% by weight of a compatible neutralised organic acid calcium sequestrant in the form of its sodium salt, the  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, and the silica, sodium oxide and sodium form of the sequestrant constituting from 40 to 55% by weight of the solution.

**[0018]** Using the high solids content (i.e. silica, sodium oxide and sodium form of the organic acid calcium sequestrant), the alkaline containing silica solution is not stable at  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratios outside the claimed range. Below ratio 1.2, metasilicate crystallises whereas above ratio 2.0 the concentrated solutions of alkaline containing silica solution containing silica solution and organic acid sequestrant in its sodium salt form instantaneously gel when brought into contact with each other, even where high shear dispersing apparatus is utilised. In some cases, the alkaline containing silica solution and the calcium sequestrant layer after their initial gelation.

**[0019]** Preferably the sodium form of the organic acid calcium sequestrant is selected from the group constituted by derivatives of amino (lower alkylene) acetic acids, homopolymers of (meth) acrylic acid, copolymers of acrylic acid with methacrylic acid, (meth) acrylamide or (meth) acrylate esters, and the copolymer of maleic acid with styrene or a vinyl ester or vinyl ether, or mixtures thereof. Examples of the derivative of amine (lower alkylene) acetic acid are ethylene diamine tetraacetic acid (EDTA), diethylene triamine penta methylene phosphonic acid (DTMP) and diethylene triamine pentaacetic acid (DTPA).

**[0020]** According to a second aspect of the invention there is provided a bleaching bath formulation comprising 5 to 25 g/litre of hydrogen peroxide, 5 to 25 g/litre of sodium hydroxide and 5 to 50 g/litre of a stabilising agent wherein the stabilising agent is an alkali containing silica solution comprising 15 to 30% by weight of silica, 10 to 25% by weight of sodium oxide, 2 to 6% by weight of a compatible neutralised organic acid calcium sequestrant in the form of its sodium salt, the  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0 (preferably 1.4 to 1.8), and the silica, sodium oxide and sodium form of the sequestrant constituting from 40 to 55% by weight of the solution.

**[0021]** According to a third aspect of the invention there is provided a process for the alkaline hydrogen peroxide bleaching of textiles wherein:

- i) 5 to 25 g/litre of hydrogen peroxide,
- ii) 5 to 25 g/litre of sodium hydroxide, and
- iii) 5 to 25 g/litre of an alkali containing silica solution comprising 15 to 30% by weight of silica, 10 to 25% by weight of sodium oxide, 2 to 6% by weight of a compatible neutralised organic acid calcium sequestrant in the form of its sodium salt, the  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0 (preferably 1.4 to 1.8), and the silica, sodium oxide and sodium form of the sequestrant constituting from 40 to 55% by weight of the solution,

are mixed together to form a bleaching bath, the bleaching process being carried out at a temperature between 80°C and 100°C, within a pH range of 10.5 to 11.5, over a period of between 20 and 90 minutes.

## Test Procedures

### 1. Alkaline Hydrogen Peroxide Bleaching

#### 1.1 Whiteness Scale Measurement

**[0022]** The bleaching liquor is made by weighing into a one litre beaker 12 g sodium hydroxide (50% w/w NaOH), 23 g silicate solution, 70 g hydrogen peroxide (35%  $\text{H}_2\text{O}_2$ ), 6 g of a wetting agent (Crosprep WCW obtained from Crosfield Group - Textiles Chemicals Division - England), diluting with water between each addition, mixing thoroughly and making up to 1000g with water. The unbleached cloth (about 10g in weight) is then soaked in the bleaching liquor and passed through a mangle to squeeze out excess liquid.

**[0023]** This operation is repeated at least twice to ensure an even liquor pick-up of 70%. Seal the cloth in a plastic bag and place in a Werner Mathis steamer for 20 minutes at 100°C. Immediately, after the steaming whilst the cloth is still "hot" wash twice with boiling water to remove any wax-type materials. Finally wash the cloth with hand hot water (in the range of 50°C to 60°C) and then with cold water. During each washing cycle the cloth is continually shaken in the washing solution. It is then ironed dry and the degree of whiteness measured using an Elrepho Reflectance Spectrometer at a wavelength of 460 nm after first standardising the instrument with magnesium oxide.

#### 1.2 Hydrogen Peroxide Decay Curve Analysis

**[0024]** The bleaching liquor is made up as stated earlier. Weigh accurately six pieces of cloth of approximately 10 g (weight  $X$ ) and soak them in the bleaching liquor. Pass the test cloths through a mangle, and repeat these soaking and squeezing operations at least twice to ensure the cloth picks up 70% of bleaching liquor. Re-weigh the cloth (weight  $Y$ ) and seal into individual plastic bags. Place five of the sealed bags containing the test cloths into a Werner Mathis steamer, setting the timer for five minute intervals. The sixth piece of cloth is immediately cut up into smaller sections and transferred to a conical flask containing 100 ml aqueous sulphuric acid ( $\approx 10\% \text{H}_2\text{SO}_4$ ). This operation prevents hydrogen peroxide decay allowing the measurement to be used for assessing the amount of hydrogen peroxide present at zero time. At five minute intervals one of the bags is removed from the steamer and the above process is repeated to "fix" the level of hydrogen peroxide remaining after the set steaming time.

**[0025]** The eluted solutions contained in the flasks are titrated against permanganate solution (0.02M) until a permanent pink colour is obtained. The amount of residual hydrogen peroxide remaining in each solution can then be determined from the following equation :

$$[\text{H}_2\text{O}_2] \text{ (ml/l)} = \frac{\text{titre} \times 4.28}{[\text{H}_2\text{O}_2] \text{ on cloth (ml)}}$$

Wherein "titre" = volume (in ml) of potassium permanganate solution used during titration and "[ $\text{H}_2\text{O}_2$ ] on cloth (ml)" is directly obtained from the difference in weight ( $Y-X$ ).

**[0026]** The data can either be presented graphically as a decay curve or in tabular form.

#### 1.3 Standardisation of Alkalinity

**[0027]** To maintain the same caustic level of the bleaching system, independent of the silicate solution under test,

the Na<sub>2</sub>O level is measured by titration with dilute hydrochloric acid. A 10 ml aliquot of the silicate solution (diluted to ≈ 5%) is titrated against 0.1M hydrochloric acid, using bromothymol blue as indicator. The amount of sodium hydroxide solution needed in the alkaline hydrogen peroxide bleaching system can then be adjusted according to the alkalinity of the silicate solution.

5

## 2. Calcium Chloride Precipitation Limit (CCPL)

**[0028]** It is essential to determine the effectiveness of the modified silicate solutions to prevent the precipitation of calcium silicate derivatives. To this end a turbidimetric method has been developed.

10 **[0029]** Approximately 1 g of silicate solution is accurately weighed into a 250 ml beaker and diluted with 50 ml of distilled water. This solution is adjusted to pH 8.0 with acetic acid and then 10 ml of dilute sodium carbonate (2% Na<sub>2</sub>CO<sub>3</sub>) followed by sufficient caustic soda solution - dropwise to attain a pH 11 (operating pH of a bleaching bath). The contents of the beaker is made up to 100 ml with distilled water.

15 **[0030]** To this stirred solution dilute calcium chloride (0.25 M) is added in 0.5 ml aliquots, and after each addition 10 ml are withdrawn, transferred to a Hach tube and the latter placed in a Hach Ratio/XR turbidimeter obtained from Cam-lab - England. The instrument is calibrated with standard cloud tubes of differing scattering intensity before the calcium precipitated solution is measured. After each measurement the contents of the Hach tube is returned to the beaker containing the test solution. If pH drifts it is readjusted to 11 by adding caustic solution drop-wise.

20 **[0031]** A graph of the volume of calcium chloride solution (0.25M) added against the turbidity measurement is used to assess where the extrapolated curve intercepts the X-axis (CCPL value) measured in ml. For each modified silicate solution a control with similar solids content and ratio (SiO<sub>2</sub>:Na<sub>2</sub>O) is used to determine the CCPL value the absence of an organic acid calcium sequestrant.

**[0032]** The difference between the CCPL for the modified silicate and that obtained for the control is the ΔCCPL, and the larger this value the greater the suppression of calcium silicate precipitation.

25

## SPECIFIC DESCRIPTION OF THE INVENTION

**[0033]** In order that the present invention may be further understood it will be described hereafter by means of examples.

30 **[0034]** In these examples parts and percentages are by weight, unless otherwise specified. When the description refers to SiO<sub>2</sub>:M<sub>2</sub>O ratios of silicate solutions, M is an alkaline metal.

### EXAMPLE 1

35 **[0035]** A number of silicate solutions with silica and metal oxide contents varying from 18% to 30%, and from 8% to 20% respectively, in the ratio range from 1.0 to 3.3, have been screened as potential stabilisers in the alkaline hydrogen peroxide bleaching system.

**[0036]** As an example of white goods plain cotton has been bleached in the bleaching liquor formula, as described in the test procedure, in which the silicate stabilising system has been varied with respect to ratio and metal oxide.

40 **[0037]** The whiteness values have been measured on the treated cloth, after bleaching for 20 minutes at 100°C in a Werner Mathis steamer. Listed below in Table 1 are the whiteness values obtained for the various silicate additions, the measurements being determined on an Elrepho spectrophotometer.

**[0038]** In addition to measuring whiteness values the hydrogen peroxide decay curves have also been measured according to the methodology described under test procedures and the data in tabular form obtained with the various silicate solutions are also given in Table 1.

45 **[0039]** Clearly the data demonstrate the effectiveness of the alkaline hydrogen peroxide bleaching system is not dependent upon the ratio of the alkaline silicate, providing the overall metal oxide concentration of the bleaching batch solution remains constant.

50

55

Table I

	Sodium Silicate					Potassium Silicate	
SiO <sub>2</sub> /M <sub>2</sub> O ratio	3.3	2.5	2.0	1.6	1.0	2.0	1.43
SiO <sub>2</sub> (% by weight)	29.50	31.10	28.05	28.75	18.58	27.45	27.85
M <sub>2</sub> O (% by weight)	8.85	12.85	14.03	17.98	19.20	13.65	17.43
Degree of Whiteness	83.0	82.5	82.5	84.0	83.0	83.9	83.7
ml of residual H <sub>2</sub> O <sub>2</sub> After:							
0 minutes	58	61	59	59	60	61	60
5 minutes	30	33	32	32	30	33	35
10 minutes	27	25	26	27	27	29	29
15 minutes	23	20	22	23	24	25	25
20 minutes	19	16	20	20	22	19	21
25 minutes	15	14	15	15	16	15	17
30 minutes	13	10	10	12	13	13	14

[0040] In general whiteness values and decay profiles are considered to be representative of a satisfactory bleaching system if the former is greater than 80, and the latter has a limiting concentration of hydrogen peroxide in the region of 10 ml of 35% H<sub>2</sub>O<sub>2</sub>.

#### EXAMPLE II

[0041] In order to determine whether it is possible to obtain homogeneous stable blends when the organic acid calcium sequestrants are mixed with alkali containing silica solutions, a range of silicate solutions with different SiO<sub>2</sub>:M<sub>2</sub>O ratios and different SiO<sub>2</sub> and M<sub>2</sub>O concentrations have been selected, together with the candidate organic acid calcium sequestering agents. These latter include:

- i) 40% solution of the sodium salt of diethylenetriamine penta acetic acid (DTPA) - Tetralon<sup>®</sup>B (supplied by Allied Colloids - England).
- ii) 40% solution of the sodium salt of diethylene triamine penta ethylene phosphonic acid (DTPMP) - Masquol<sup>®</sup>P 550 (supplied by Protex - England).
- iii) 40% solution of the sodium salt of a copolymer of acrylic acid and maleic acid having an average molecular weight of 20,000 - Alcosperse<sup>®</sup>175 (supplied by National Starch - England)

[0042] The blends have been prepared by adding the candidate neutralised organic acid calcium sequestrant (40% solution as its sodium salt) to the stirred alkali containing silica solution. After aeration has settled, caused by the mixing action of the stirrer, the blends are transferred to a glass sample bottle and sealed to prevent moisture escaping. The blends have been stored for up to a period of 3-months at ambient temperature. The observations recorded in Table II are on the blends after standing for one month.

TABLE II

SiO <sub>2</sub> /M <sub>2</sub> O Weight Ratio		Sodium Silicate					Potassium Silicate	
		3.3	2.5	1.6	1.2	1.0	2.0	1.43
Organic Acid	Alcosperse <sup>®</sup> 175	layered	layered	clear	clear	crystalises	layered	solid

TABLE II (continued)

SiO <sub>2</sub> /M <sub>2</sub> O Weight Ratio		Sodium Silicate					Potassium Silicate	
		3.3	2.5	1.6	1.2	1.0	2.0	1.43
Calcium Sequestrant at 10% addition	DTPA	layered	clear	clear	clear	crystalises	cloudy	solid
	DTPMP	v. viscous	clear	clear	clear	crystalises	solid	solid

[0043] The data demonstrates a range of stability for blends prepared from alkali containing silicate solutions with a weight ratio SiO<sub>2</sub>/M<sub>2</sub>O of 1.2 to 2.0 and organic acid calcium sequestrants up to a concentration of 10% as the 40% solution of their sodium salt, i.e. 4% as the anhydrous material.

### EXAMPLE III

[0044] Following the procedure outlined in Example II a further series of compatibility tests have been carried out but in this case, for two SiO<sub>2</sub>/M<sub>2</sub>O ratios (1.6 and 2.0), the level of organic acid calcium sequestrant has been varied from 0.8 to 10% on an anhydrous basis. The observations are recorded in Table III on the blends after standing for one month, and the data shows the range of compatibility can be extended for sodium silicate solutions with a SiO<sub>2</sub>/Na<sub>2</sub>O weight ratio of 1.6 and 2.0 respectively, to include an organic acid calcium sequestrant concentration of 0.8 to 10%, even when Alcosperse<sup>®</sup>175 is utilised in the formulation.

[0045] Though the latter at 10% concentration (anhydrous basis) is extremely cloudy in appearance it did not separate into two layers on standing.

TABLE III

		% Organic Acid Sequestrant (Anhydrous)		
		0.8	4	10
Compatibility with SiO <sub>2</sub> /Na <sub>2</sub> O weight ratio of 2	Alcosperse <sup>®</sup> 175	clear	turbid	cloudy
	DTPA	clear	clear	clear
	DTPMP	clear	clear	clear
Compatibility with SiO <sub>2</sub> /Na <sub>2</sub> O weight ratio of 1.6	Alcosperse <sup>®</sup> 175	clear	clear	cloudy
	DTPA	clear	clear	clear
	DTPMP	clear	clear	clear

### EXAMPLE IV

[0046] In the examples given above it has been demonstrated that organic acid calcium sequestrants in form of a 40% solution of their sodium salt are compatible with alkali containing silica solutions, particularly in the SiO<sub>2</sub>/M<sub>2</sub>O ratio range of 1.2 to 2.0. It has also been shown that silicate solutions in this ratio range will stabilise alkaline hydrogen peroxide bleaching systems and there is no detrimental effect on the whiteness of the cloth obtained.

[0047] The objective of this example is to show that the modified alkali containing silica solutions have a greater propensity to minimise the precipitation of calcium silicates than their parent silicate solutions. A test has been developed to monitor the extent of calcium precipitation. The test is based on measuring the increasing turbidity of a model bleaching system where a solution of calcium chloride is added to the diluted alkali containing silica solution at pH 11. The larger ΔCCPL the greater the extent of calcium ion suppression.

[0048] The CCPL's for the range of modified alkali containing silica solutions containing 4% of the sequestrant in the form of its sodium salt, in the ratio range 1.6 to 2.0 are given in Table IV.

TABLE IV

SiO <sub>2</sub> /Na <sub>2</sub> O weight ratio	Na Silicate		
		2.0	1.6
Value of ΔCCPL for modifies silicates with 10% additions in ml.	Alco	0.95	1.45
	DTPA	0.6	0.75
	DTPMP	0.80	1.20

[0049] It can be seen that the most effective organic acid calcium sequestrant for suppressing the precipitation of calcium silicates is Alcosperse<sup>®</sup>175.

#### EXAMPLE V

[0050] In the Example IV it has been demonstrated that the modified alkali containing silica solution in the ratio range 1.6 to 2.0 containing 4% organic acid calcium sequestrant, in the form of its sodium salt, suppresses the precipitation of calcium silicates. Clearly, the major application for a silicate solution exhibiting this inhibitive behaviour would be as a stabiliser in the alkaline hydrogen peroxide bleaching system.

[0051] In accordance with the methodology described in Example I hydrogen peroxide decay curves and whiteness tests have been carried out using the modified alkali containing silica solutions. The data obtained from the range of modified silicates is summarised in Table V. It clearly shows that provided the metal oxide content of the bleaching bath solution is maintained at the optimum level there is no detrimental effect on the cloth whiteness and the remainder concentration of hydrogen peroxide is unaffected.

TABLE V

		Organic Acid Calcium Sequestrant at 10%						No Sequestrant	
		Alcosperse		DTPA		DTPMP			
SiO <sub>2</sub> /Na <sub>2</sub> O weight ratio		2.0	1.6	2.0	1.6	2.0	1.6	2.0	1.6
% Whiteness		83.5	83.5	83.8	83.2	83.7	82.5	82.5	84.0
Residual amount of H <sub>2</sub> O <sub>2</sub> in ml on cloth after various time intervals (minutes)	0	59	59	60	60	60	60	59	59
	5	28	31	38	34	32	32	32	32
	10	23	23	29	27	27	28	26	27
	15	18	18	26	27	23	23	22	23
	20	16	16	15	21	20	19	10	20
	25	13	14	14	19	16	16	15	15
	30	10	10	13	14	13	13	10	12

#### Claims

- Alkali containing silica solution comprising 15 to 30% by weight of silica, 10 to 25% by weight of sodium oxide, 2 to 6% by weight of a compatible neutralised organic acid calcium sequestrant in the form of its sodium salt, the SiO<sub>2</sub>/Na<sub>2</sub>O weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, and the silica, sodium oxide and sodium form of the sequestrant constituting from 40 to 55% by weight of the solution.
- Alkali containing silica solution according to Claim 1 wherein the sodium form of the organic acid calcium sequestrant is selected from the group constituted by derivatives of amino (lower alkylene) acetic acids, homopolymers of (meth) acrylic acid, copolymers of acrylic acid with methacrylic acid, (meth) acrylamide or (meth) acrylate esters, and the copolymer of maleic acid with styrene or a vinyl ester or vinyl ether, or mixtures thereof.

3. Alkali containing silica solution according to Claim 2 in which the derivative of amine (lower alkylene) acetic acid is selected from ethylene diamine tetraacetic acid, diethylene triamine penta methylene phosphonic acid and diethylene triamine pentaacetic acid.
- 5 4. A bleaching bath formulation comprising 5 to 25 g/litre of hydrogen peroxide, 5 to 25 g/litre of sodium hydroxide and 5 to 50 g/litre of a stabilising agent wherein the stabilising agent is an alkali containing silica solution comprising 15 to 30% by weight of silica, 10 to 25% by weight of sodium oxide, 2 to 6% by weight of a compatible neutralised organic acid calcium sequestrant in the form of its sodium salt, the  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, and the silica, sodium oxide and sodium form of the sequestrant constituting from 40 to 55% by weight of the solution.
- 10
5. Process for the alkaline hydrogen peroxide bleaching of textiles wherein:
- i) 5 to 25 g/litre of hydrogen peroxide,  
 15 ii) 5 to 25 g/litre of sodium hydroxide, and  
 iii) 5 to 25 g/litre of an alkali containing silica solution comprising 15 to 30% by weight of silica, 10 to 25% by weight of sodium oxide, 2 to 6% by weight of a compatible neutralised organic acid calcium sequestrant in the form of its sodium salt, the  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, and the silica, sodium oxide and sodium form of the sequestrant constituting from 40 to 55% by weight of the solution,
- 20
- are mixed together to form a bleaching bath, the bleaching process being carried out at a temperature between 80°C and 100°C, within a pH range of 10.5 to 11.5, over a period of between 20 and 90 minutes.
- 25 6. A solution, formulation or process according to any one of Claims 1 to 5 in which said  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio is up to 1.8.
7. A solution, formulation or process according to any one of Claims 1 to 5 in which said  $\text{SiO}_2/\text{Na}_2\text{O}$  weight ratio is in the range 1.4 to 1.8.
- 30

### Patentansprüche

1. Alkali enthaltende Siliciumoxidlösung, die 15 bis 30 Gew.-% Siliciumoxid, 10 bis 25 Gew.-% Natriumoxid, 2 bis 6 Gew.-% eines kompatiblen Calcium-Sequestrierungsmittels vom Typ einer neutralisierten organischen Säure in der Form seines Natriumsalzes umfaßt, wobei das  $\text{SiO}_2/\text{Na}_2\text{O}$ -Gewichtsverhältnis der Alkali enthaltenden Siliciumoxidlösung im Bereich von 1.2 bis 2.0 liegt, und das Siliciumoxid, das Natriumoxid und die Natriumform des Sequestrierungsmittels 40 bis 55 Gew.-% der Lösung ausmachen.
- 35
2. Alkali enthaltende Siliciumoxidlösung nach Anspruch 1, wobei die Natriumform des Calcium-Sequestrierungsmittels vom Typ einer organischen Säure ausgewählt ist aus der Gruppe, die aus Derivaten von Amino(niederalkylen)essigsäuren, Homopolymeren von (Meth)acrylsäure, Copolymeren von Acrylsäure mit Methacrylsäure, (Meth)acrylamid oder (Meth)acrylatestern und dem Copolymer aus Maleinsäure mit Styrol oder einem Vinylester oder Vinylether, oder Mischungen davon besteht.
- 40
3. Alkali enthaltende Siliciumoxidlösung gemäß Anspruch 2, bei der das Amino(niederalkylen)essigsäure-Derivat ausgewählt ist aus Ethylendiamintetraessigsäure, Diethylentriaminpentamethylenphosphonsäure und Diethylentriaminpentaessigsäure.
- 45
4. Bleichbadformulierung, die 5 bis 25 g/liter Wasserstoffperoxid, 5 bis 25 g/liter Natriumhydroxid und 5 bis 50 g/liter eines Stabilisierungsmittels umfaßt, wobei das Stabilisierungsmittel eine Alkali enthaltende Siliciumoxidlösung ist, die 15 bis 30 Gew.-% Siliciumoxid, 10 bis 25 Gew.-% Natriumoxid, 2 bis 6 Gew.-% eines kompatiblen Calcium-Sequestrierungsmittels vom Typ einer neutralisierten organischen Säure in der Form seines Natriumsalzes umfaßt, wobei das  $\text{SiO}_2/\text{Na}_2\text{O}$ -Gewichts-Verhältnis der Alkali enthaltenden Siliciumoxidlösung im Bereich von 1,2 bis 2,0 liegt und das Siliciumoxid, das Natriumoxid und die Natriumform des Sequestrierungsmittels 40 bis 55 Gew.-% der Lösung ausmachen.
- 50
5. Verfahren zum alkalischen Wasserstoffperoxidbleichen von Textilien, bei dem
- 55

(i) 5 bis 25 g/liter Wasserstoffperoxid,

(ii) 5 bis 25 g/liter Natriumhydroxid, und

(iii) 5 bis 25 g/liter einer Alkali enthaltenden Siliciumoxidlösung, die 15 bis 30 Gew.-% Siliciumoxid, 10 bis 25 Gew.-% Natriumoxid, 2 bis 6 Gew.-% eines kompatiblen Calcium-Sequestrierungsmittels vom Typ einer neutralisierten organischen Säure in Form seines Natriumsalzes umfaßt, wobei das  $\text{SiO}_2/\text{Na}_2\text{O}$ -Gewichtsverhältnis der Alkali enthaltenden Siliciumoxidlösung im Bereich von 1.2 bis 2.0 liegt und das Siliciumoxid, das Natriumoxid und die Natriumform des Sequestrierungsmittels 40 bis 55 Gew.-% der Lösung ausmachen,

miteinander vermischt werden, um ein Bleichbad zu bilden, wobei das Bleichverfahren bei einer Temperatur zwischen 80°C und 100°C innerhalb eines pH-Bereichs von 10,5 bis 11,5 und innerhalb eines Zeitraums von 20 bis 90 Minuten durchgeführt wird.

6. Eine Lösung, eine Formulierung oder ein Verfahren nach irgendeinem der Ansprüche 1 bis 5, wobei das  $\text{SiO}_2/\text{Na}_2\text{O}$ -Gewichtsverhältnis bis zu 1.8 beträgt.

7. Eine Lösung, eine Formulierung oder ein Verfahren nach irgendeinem der Ansprüche 1 bis 5, wobei das  $\text{SiO}_2/\text{Na}_2\text{O}$ -Gewichtsverhältnis im Bereich von 1.4 bis 1.8 liegt.

### Revendications

1. Solution alcaline de silice comprenant 15% à 30% en poids de silice, 10% à 25% en poids d'oxyde de sodium, 2% à 6% en poids d'un agent séquestrant de calcium d'acide organique neutralisé compatible sous la forme de son sel de sodium, le rapport pondéral  $\text{SiO}_2/\text{Na}_2\text{O}$  de la solution alcaline de silice se situant dans la plage de 1,2 à 2,0 et la silice, l'oxyde de sodium et la forme sodique de l'agent séquestrant constituant 40% à 55% en poids de la solution.

2. Solution alcaline de silice selon la revendication 1, dans laquelle la forme sodique de l'agent séquestrant de calcium d'acide organique est sélectionnée dans le groupe constitué de dérivés d'acides amino(alkylène inférieur)acétiques, d'homopolymères d'acide (méth)acrylique, de copolymères d'acide acrylique et d'acide méthacrylique, de (méth)acrylamide ou d'esters de (méth)acrylate, et du copolymère d'acide maléique et de styrène ou d'un ester ou d'un éther vinylique, ou de leurs mélanges.

3. Solution alcaline de silice selon la revendication 2, dans laquelle le dérivé de l'acide amino(alkylène inférieur)acétique est choisi parmi l'acide éthylènediaminetétraacétique, l'acide diéthylènetriaminepentaméthylène phosphonique et l'acide diéthylènetriaminepentaacétique.

4. Formulation de bain de blanchiment comprenant 5 à 25 g/litre de peroxyde d'hydrogène, 5 à 25 g/litre d'hydroxyde de sodium et 5 à 50 g/litre d'un agent stabilisateur, dans laquelle l'agent stabilisateur est une solution alcaline de silice comprenant 15% à 30% en poids de silice, 10% à 25% en poids d'oxyde de sodium, 2% à 6% en poids d'un agent séquestrant de calcium d'acide organique neutralisé compatible sous la forme de son sel de sodium, le rapport pondéral  $\text{SiO}_2/\text{Na}_2\text{O}$  de la solution alcaline de silice se situant dans la plage de 1,2 à 2,0 et la silice, l'oxyde de sodium et la forme sodique de l'agent séquestrant constituant 40% à 55% en poids de la solution.

5. Procédé de blanchiment de textiles au peroxyde d'hydrogène alcalin, dans lequel :

i) 5 à 25 g/litre de peroxyde d'hydrogène,

ii) 5 à 25 g/litre d'hydroxyde de sodium, et

iii) 5 à 25 g/litre d'une solution alcaline de silice comprenant 15% à 30% en poids de silice, 10% à 25% en poids d'oxyde de sodium, 2% à 6% en poids d'un agent séquestrant de calcium d'acide organique neutralisé compatible sous la forme de son sel de sodium, le rapport pondéral  $\text{SiO}_2/\text{Na}_2\text{O}$  de la solution alcaline de silice se situant dans la plage de 1,2 à 2,0 et la silice, l'oxyde de sodium et la forme sodique de l'agent séquestrant constituant 40% à 55% en poids de la solution,

sont mélangés ensemble pour former un bain de blanchiment, le processus de blanchiment s'effectuant à une température entre 80°C et 100°C, dans une plage de pH de 10,5 à 11,5, sur une période de 20 à 90 minutes.

**EP 0 585 038 B1**

6. Solution, formulation ou procédé selon l'une quelconque des revendications 1 à 5, dans lesquels ledit rapport pondéral  $\text{SiO}_2/\text{Na}_2\text{O}$  va jusqu'à 1,8.
7. Solution, formulation ou procédé selon l'une quelconque des revendications 1 à 5, dans lesquels ledit rapport pondéral  $\text{SiO}_2/\text{Na}_2\text{O}$  se situe dans la plage de 1,4 à 1,8.

10

15

20

25

30

35

40

45

50

55