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(54) Alkali containing silica solution.

(57) An alkali containing silica solution comprising 15% to 30% by weight of silica, 10% to 25% by weight of potassium or sodium oxide or mixtures thereof, 2% to 6% by weight of a compatible neutralised organic acid calcium sequestrant the SiO_2/Na_2O ratio of the alkali containing silica solution being in the range 1.2 to 2.0 has been found to be a suitable stabilizer for alkaline hydrogen peroxide bleaching of textiles.

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Field of the Invention

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

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).

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.

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.

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.

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.

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.

Simplifying the complexity of the alkaline hydrogen peroxide bleaching process gives the Textile Mill added commercial advantages in the reduction of infantry 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

The use of sodium silicate having a SiO_2/Na_2O 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 2,838, 459 (Pennalt Chemicals Corp.). In US 3,391,594, (Pennalt Chemicals Corp.) the SiO_2/Na_2O 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.

The metal oxide associated with the silicate is usually Na_2O. However, in US 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 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.).

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 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.

It has now been found that, within a selected SiO_2/Na_2O weight ratio, alkali containing silica solutions can be made compatible with the neutralised form of organic acid calcium sequestrants even at high SiO_2 concentration. It has been demonstrated that these alkali 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

It is a first object of the present invention to provide an alkali containing silica solution comprising 15% to 30% by weight of silica, preferably 20% to 30% by weight of silica, 10% to 25% by weight of potassium or sodium oxide or mixtures thereof, 2 to 6% by weight of a compatible neutralised organic acid calcium sequestrant, preferably in the form of its sodium salt, the SiO_2/Na_2O weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, preferably 1.4 to 1.8.

At high solids content (i.e. silica, metal oxide and sodium form of the organic acid calcium sequestrant), usually in the range 40% to 55% by weight, the alkali containing silica solution is not stable at SiO_2/Na_2O ratios outside the claimed range. Below ratio 1.2, metasilicate crystallises, particularly with alkali containing silica solutions comprising Na_2O as the alkaline metal oxide, whereas above ratio 2.0 the concentrated solutions of alkali 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 alkali containing silica solution and the calcium sequestrant layer after their initial gelation.

Preferably, the organic acid calcium sequestrant is selected in the group constituted by, derivatives of amino (lower alkaline) acetic acids for example ethylene tetraacetic acid (EDTA), diethylene triamine penta methylene phosphonic acid (DTMP) and diethylene triamine pentaacetic acid (DTPA), or from homopolymer of (meth)acrylic acid or copolymer of acrylic acid with methacrylic acid (meth) acrylamide, (meth) acrylate esters and the copolymer of maleic acid with styrene or a vinyl ester of vinyl ether, or mixtures thereof.

It is a second object of the present invention to provide for 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 system wherein the stabilising system is an alkali containing silica solution, comprising 15% to 30% by weight of silica, preferably 20% to 30% by weight of silica, 10% to 25% by weight of potassium or sodium oxide or mixtures thereof, 2% to 6% by weight of a compatible neutralised organic acid calcium sequestrant, preferably in the form of its sodium salt, the SiO_2/Na_2O weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, preferably 1.4 to 1.8.

It is a third object of the present invention to provide for 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,

iii) and 5 to 25 g/litre of an alkali containing silica solution comprising 15% to 30% by weight of silica, preferably 20% to 30% by weight of silica, 10% to 25% by weight of potassium or sodium oxide or mixtures thereof, 2% to 6% by weight of a compatible neutralised organic acid calcium sequestrant, preferably in the form of its sodium salt, the SiO_2/Na_2O weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, preferably 1.4 to 1.8,

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

Test Procedures

1. Alkaline Hydrogen Peroxide Bleaching

1.1 Whiteness Scale Measurement

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% H_2O_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.

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

The bleaching liquor is made up as stated earlier. Weigh accurately six pieces of cloth of approximately 10 g (weight $\underline{X}$) 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 $\underline{Y}$) 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 (≈ 10% H_2SO_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.

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 :

$$[H_2O_2]\ (\text{ml/l}) = \frac{\text{titre x } 4.28}{[H_2O_2]\ \text{on cloth (ml)}}$$

Wherein "titre" = volume (in ml) of potassium permanganate solution used during titration and "$[H_2O_2]$ on cloth (ml)" is directly obtained from the difference in weight ($\underline{Y}$-$\underline{X}$).

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

1.3 Standardisation of Alkalinity

To maintain the same caustic level of the bleaching system, independent of the silicate solution under test, the Na_2O 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.

2. Calcium Chloride Precipitation Limit (CCPL)

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.

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_2CO_3) 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.

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 Hatch tube and the latter placed in a Hatch Ratio/XR turbidimeter obtained from Camlab - 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 Hatch tube is returned to the beaker containing the test solution. If pH drifts it is readjusted to 11 by adding caustic solution drop-wise.

A graph of the volume of sodium 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_2:Na_2O) is used to determine the CCPL value the absence of an organic acid calcium sequestrant.

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.

SPECIFIC DESCRIPTION OF THE INVENTION

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

In these examples parts and percentages are by weight, unless otherwise specified. When the description refers to SiO_2:M_2O ratios of silicate solutions, M is an alkaline metal.

EXAMPLE 1

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.

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.

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.

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.

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.

Table I

	Sodium Silicate					Potassium Silicate	
SiO_2/M_2O ratio	3.3	2.5	2.0	1.6	1.0	2.0	1.43
SiO_2 (% by weight)	29.50	31.10	28.05	28.75	18.58	27.45	27.85
M_2O (% 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_2O_2 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

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_2O_2.

EXAMPLE II

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_2:M_2O ratios and different SiO_2 and M_2O 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®B (supplied by Allied Colloids - England).

ii) 40% solution of the sodium salt of diethylene triamine penta ethylene phosphonic acid (DTPMP) - Masquol®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®175 (supplied by National Starch - England)

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

		Sodium Silicate					**Potassium Silicate**	
SiO_2/M_2O Weight Ratio		**3.3**	**2.5**	**1.6**	**1.2**	**1.0**	**2.0**	**1.43**
Organic Acid	Alcosperse ® 175	layered	layered	clear	clear	crystalises	layered	solid
Calcium Sequestrant at 10% addition	DTPA	layered	clear	clear	clear	crystalises	cloudy	solid
	DTPMP	v. viscous	clear	clear	clear	crystalises	solid	solid

The data demonstrates a range of stability for blends prepared from alkali containing silicate solutions with a weight ratio SiO_2/M_2O 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

Following the procedure outlined in Example II a further series of compatibility tests have been carried out but in this case, for two SiO_2/M_2O 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_2/Na_2O 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®175 is utilised in the formulation.

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_2/Na_2O weight ratio of 2	Alcosperse ® 175	clear	turbid	cloudy
	DTPA	clear	clear	clear
	DTPMP	clear	clear	clear
Compatibility with SiO_2/Na_2O weight ratio of 1.6	Alcosperse ® 175	clear	clear	cloudy
	DTPA	clear	clear	clear
	DTPMP	clear	clear	clear

EXAMPLE IV

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_2/M_2O 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.

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.

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

	Na Silicate		
$Si0_2/Na_20$ weight ratio		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

It can be seen that the most effective organic acid calcium sequestrant for suppressing the precipitation of calcium silicates is Alcosperse®175.

EXAMPLE V

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.

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_2/Na_2O 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_2O_2 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

1. Alkali containing silica solution comprising 15% to 30% by weight of silica, 10% to 25% by weight of potassium or sodium oxide or mixtures thereof, 2% to 6% by weight of a compatible neutralised organic acid calcium sequestrant, the SiO_2/Na_2O weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0.

2. Alkali containing silica solution according to claim 1 wherein the organic acid calcium sequestrant is selected in the group constituted by, derivatives of amino (lower alkaline) acetic acids for example ethylene tetraacetic acid , diethylene triamine penta methylene phosphonic acid and diethylene triamine pentaacetic acid, or from homopolymer of (meth)acrylic acid or copolymer of acrylic acid with methacrylic acid (meth) acrylamide, (meth) acrylate esters and the copolymer of maleic acid with styrene or a vinyl ester of vinyl ether, or mixtures thereof.

3. 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 system wherein the stabilising system is an alkali containing silica solution, comprising 15% to 30% by weight of silica, 10% to 25% by weight of potassium or sodium oxide or mixtures thereof, 2% to 6% by weight of a compatible neutralised organic acid calcium sequestrant, the SiO_2/Na_2O weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0.

4. 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,
   iii) and 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 potassium or sodium oxide or mixtures thereof, 2% to 6% by weight of a compatible neutralised organic acid calcium sequestrant the SiO_2/Na_2O weight ratio of the alkali containing silica solution being in the range 1.2 to 2.0, are mixed together to form a bleaching bath, the bleaching process being carried out at a temperature between 80°C and 100°C, within the pH range 10.5 to 11.5, over a period of between 20 to 90 minutes.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 6496

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 210 952 (CIBA-GEIGY) * page 11, line 8 - line 19; claims 1-12,17,20; examples 5-6 * ---	1-4	C11D3/08 C11D3/39 D06L3/02 C11D7/14
X	EP-A-0 407 626 (HENKEL) * page 2, line 48 - page 3, line 22; claim 1; examples 1-4 * ---	1,2	
A	FR-A-2 643 093 (MANUFACTURE DE PRODUITS CHIMIQUES PROTEX) * claims 1,7; examples 1-4 * ---	1-4	
A	DE-A-21 47 300 (PROCTER & GAMBLE) * claims 1-4 * ---	1,2	
D,A	US-A-2 838 459 (O.S. SPROUT) * claims; examples * ---	1-4	
A	US-A-3 449 254 (R.N. SUITER) * claims * ---	1-4	
A	US-A-3 150 918 (R.R. CURRIER) * column 2, line 54 - column 3, line 26; claims; examples * ---	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C11D D06L
A	GB-A-1 123 071 (BOWMANS CHEMICALS LTD.) * example * ---	1-4	
A	GB-A-923 897 (LAPORTE CHEMICALS LTD.) * column 2, line 25 - line 31; claims; examples * -----	1-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 November 1993	GRITTERN, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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