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(54) Title: A PROCESS FOR PROVIDING LOCALIZED VARIATION IN THE COLOUR DENSITY OF FABRICS

(57) Abstract

Process for providing improved localised variation in the colour density of the surface of dyed fabrics, the process comprising treating a dyed fabric with a cellulytic enzyme in an aqueous liquor comprising a di- or trivalent cation and a chelating agent in a molar ratio of 1:0.1-50.

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A PROCESS FOR PROVIDING LOCALIZED VARIATION IN THE COLOUR DENSITY OF FABRICS

FIELD OF INVENTION

The present invention relates to processes of providing localized variation in the colour of dyed fabrics.

BACKGROUND OF THE INVENTION

The most usual method of providing a "stone-washed" look (localized abrasion of the colour) in dyed fabrics, in particular cellulose-containing fabrics, is by washing cellulose-containing fabrics or clothing made from such fabrics in the presence of pumice stones to provide the desired localized lightening of the colour of the fabric. Using pumice for this purpose has the disadvantage that pumice particles have to be washed from the fabric or clothing subsequently to treatment, and that the pumice stones and particles cause a significant wear of the machines used in the process. Also, handling large amounts of stones may be a problem.

Other approaches to providing a "stone-washed" appearance to fabrics have therefore been suggested. For instance, enzymes, in particular cellulytic enzymes, have been suggested for this purpose, either alone (4,832,864) or together with a smaller amount of pumice than required in the traditional process.

SUMMARY OF THE INVENTION

The present invention is based on the surprising finding that it is possible to obtain improved utilization of the ability of cellulytic enzymes to provide localized colour variations in dyed fabrics either by adding a chelating agent to a wash liquor containing calcium ions and other di- or trivalent cations, or by carrying out the process in soft water.

Accordingly, the present invention relates to a process for providing improved localised variation in the colour density of the surface of dyed fabrics, the process comprising treating a dyed fabric with a cellulytic enzyme in an aqueous liquor comprising a di- or trivalent cation and a chelating agent in a molar ratio of 1:0.1-50.

In another aspect, the present invention relates to a process for providing improved localised variation in the colour density of the surface of dyed fabrics, the process comprising treating a dyed fabric with a cellulytic enzyme in an aqueous liquor comprising less than 20 mg/l of Ca^{2+} and Mg^{2+}.

In the present context, the expression "improved localized variation" is intended to indicate that the differences between lighter and darker areas of the fabrics is more pronounced than in fabrics treated by the enzymatic process described in, e.g. US 4,832,864. It has been found that in the known enzymatic "stone-washing" processes for obtaining localized colour variations, at least some (though not all) of the dye washed from the fabric is redeposited thereon so that the difference between darker and lighter shades on the fabric is somewhat obscured (this phenomenon is known as backstaining to people skilled in the art). It has surprisingly been found that by reducing the amount of free calcium or other di- or trivalent cations in the liquor in which the fabric is treated (e.g. by the addition of a chelating agent to calcium-containing water or by using soft water), such redeposition of dye may be significantly reduced.

DETAILED DESCRIPTION OF THE INVENTION

The di- or trivalent cations present in the wash liquor may be alkaline earth metal ions, in particular Ca^{2+} or Mg^{2+}. According to the invention, the molar ratio between di- or trivalent ions and chelating agent depends on the nature of the chelating agent. However, a currently preferred ratio of di- or trivalent cations (such as Ca^{++}) to chelating agent is 1:0.1-10, more preferably 1:0.2-5.

Fabrics:

The process of the invention is most beneficially applied to cellulose-containing fabrics, such as cotton, viscose, rayon, ramie, linen, Tencel or mixtures thereof, or mixtures of any of of these fibres with synthetic fibres. In particular, the fabric is denim. The fabric may be dyed with vat dyes such as indigo, direct dyes such as Direct Red 185, sulphur dyes such as Sulfur Green 6, or reactive dyes fixed to a binder on the fabric surface.. In a most preferred embodiment of the present process, the fabric is indigo-dyed denim, including clothing items manufactured therefrom.

Cellulytic enzymes:

The cellulytic enzyme employed in the process of the invention may be any cellulase previously suggested for this purposes (e.g. as described in US 4,832,864). Thus, the cellulytic enzyme may be a fungal or bacterial cellulase. According to the invention, it has been found that both acid and neutral or alkaline cellulases may be employed (the selection of the chelating agent will, however, depend on the type of cellulase used). Examples of suitable acid cellulases are those derivable from a strain of Trichoderma, Irpex, Clostridium or Thermocellum sp. Examples of suitable neutral or alkaline cellulases are those derivable from a strain of Humicola, Fusarium, Bacillus, Cellulomonas, Pseudomonas, Myceliophthora or

Phanerochaete sp. Preferred cellulases may be obtained from Humicola insolens. A currently preferred cellulase is a 43 kD endoglucanase obtainable from Humicola insolens (e.g. described in WO 91/17243).

Chelating agent:

According to the present invention, the chelating agent may be one which is soluble and capable of forming complexes with di- or trivalent cations (such as calcium) at acid, neutral or alkaline pH values. As indicated above, the choice of chelating agent depends on the cellulase employed in the process. Thus, if an acid cellulase is included, the chelating agent should be one which is soluble and capable of forming a complex with di- or trivalent cations at an acid pH. If, on the other hand, the cellulase is neutral or alkaline, the chelating agent should be one which is soluble and capable of forming a complex with di- or trivalent cations at a neutral or alkaline pH.

The chelating agent may suitably be selected from aminocarboxylic acids; hydroxyaminocarboxylic acids; hydroxycarboxylic acids; phosphates, di-phosphates, tri-polyphosphates, higher poly-phosphates, pyrophosphates; zeolites; polycarboxylic acids; carbohydrates, including polysaccharides; hydroxypyridinones; organic compounds comprising catechol groups; organic compounds comprising hydroxymate groups; silicates; or polyhydroxysulfonates.

When the chelating agent is an aminocarboxylic acid, it may suitably be selected from EDTA (ethylene diamine tetra-acetic acid), DTPA (diethylene triamine pentaacetic acid), NTA (nitrilo triacetic acid), CDTA (trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid), EGTA (ethyleneglycol-O,O'-bis(2-aminoethyl)-N,N,N',N'-

tetraacetic acid), or TTHA (triethylenetetraamine-N,N,N',N'-hexaacetic acid).

When the chelating agent is a hydroxyaminocarboxylic acid, it may suitably be selected from HEDTA (hydroxyethylene diamine triacetic acid), DEG/DHEG (dihydroxyethyl glycine), or HEIDA (N-(2-hydroxyethyl)-iminodiacetat).

When the chelating agent is a hydroxycarboxylic acid, it may suitably be selected from gluconic acid, citric acid, tartaric acid, oxalic acid, diglycolic acid, or glucoheptonate.

When the chelating agent is a polyamino- or polyhydroxy-phosphonate or -polyphosphonate, it may suitably be selected from PBTC (phosphonobutantriacetat), ATMP (aminotri(methylenphosphonic acid)), DTPMP (diethylene triaminpenta(methylenphosphonic acid), EDTMP ethylene diamintetra(methylenphophonic acid)), HDTMP (hydroxyethyl-ethylendiamintri(methylenphosphonic acid)), HEDP (hydroxyethane diphosphonic acid), or HMDTMP (hexamethylen-diamine tetra(methylene phosphonic acid)).

When the chelating agent is a polycarboxylic acid (or a mixture of polycarboxylic acids), it may suitably be selected from water soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acxid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalonic acid; carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentanetetracarboxylate, phloroglucinol trisulfonate; polyacetal carboxylates.

Suitably polycarboxylic acids may be selected from polyacrylate, polymaleate, maleic-methylvinylether-copolymers, maleic-acrylic-copolymers, maleic-olefine-copolymers, polyvinylpyrrolidone, polyoxymethylcarboxylates, poly(ó-hydroxy-acrylate), poly[(3-hydroxymethyl)-hexamethylene-1,3,5-tricarboxyl], poly[(3-oxymethyl)-hexamethylene-1,3,5-tricarboxyl],poly-[(4-methoxy)-tetramethylene-1,2-dicarboxylate], poly-(tetramethylene-1,2-dicarboxylate), poly(vinyl methyl ether-maleic anhydride), MW 20.000-80.000, carboxymethyloxymalonate, carboxymethyloxysuccinate, or 1,2,3,4-Cyclopentane-tetracarboxylic acid.

Buffer:

It has been experimentally established that particularly advantageous results may be obtained in the process of the invention when the wash liquor additionally comprises a buffer.

The buffer may suitably be a phosphate, borate, citrate, acetate, adipate, triethanolamine, monoethanolamine, diethanolamine, carbonate (especially alkali metal or alkaline earth metal, in particular sodium or potassium carbonate, or ammonium and HCl salts), diamine, especially diaminoethane, imidazole, or amino acid buffer.

Dispersing agent:

Likewise, it has been experimentally established that particularly favourable results may be obtained in the process of the invention when the wash liquor additionally comprises a dispersing agent.

The dispersing agent may suitably be selected from nonionic, anionic, cationic, ampholytic or zwitterionic surfactants. More specifically, the dispersing agent may be selected from carboxymethylcellulose, hydroxypropylcellulose, alkyl aryl sulphonates, long-chain alcohol sulphates (primary and secondary alkyl sulphates), sulphonated olefins, sulphated monoglycerides, sulphated ethers, sulphosuccinates, sulphonated methyl ethers, alkane sulphonates, phosphate esters, alkyl isethionates, acyl sarcosides, alkyl taurides, fluorosurfactants, fatty alcohol and alkylphenol condensates, fatty acid condensates, condensates of ethylene oxide with an amine, condensates of ethylene oxide with an amide, block polymers (polyethylene glycol, polypropylene glycol, ethylene diamine condensed with ethylene or propylene oxide), sucrose esters, sorbitan esters, alkyloamides, fatty amine oxides, ethoxylated monoamines, ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof.

The invention is illustrated in further detail in the following example.

Example 1

Backstaining on treating denim fabric with a H. insolens 43 kD cellulase preparation was determined at three different levels of Ca^{2+} and different concentrations of EDTA. The Launder-O-Meter model was used in all trials. In each of the five trials, the Ca^{2+} concentration was kept constant in all 20 beakers. Three levels of Ca^{2+} were used.

25 mg Ca^{2+}/l (two identical trials)
100 mg Ca^{2+}/l (two trials, different EDTA/Ca^{2+} ratios)
200 mg Ca^{2+}/l (one trial)

The trials were run under the following conditions:

Temperature:	55°C
Time:	120 minutes
Fabric:	5.0 g of Swift denim, 2 swatches (approx. 7 x 7 cm) of white mercerizised 100% cotton

Mechanical effect:	1 large rubber ball
Enzyme:	SP 492: <u>Humicola insolens</u> 43 kD endoglucanase (cf. WO 91/17243), approx. 0.46 g/beaker (about 100 ECU*/beaker)
Liquid:	150 ml

Standard solutions of 20 mg Ca^{2+}/ml (as $CaCl_2.2H_2O$) and 0.6 M EDTA (sodium salt, pH 7) were prepared and used in all the trials.

Amounts of the Ca^{2+} and EDTA solutions calculated to give the desired molar ratios of Ca^{2+} to EDTA were pipetted into a glass beaker, and distilled water was added to 500 ml followed by mixing. The mixture was heated to 55-60°C for 20-30 minutes and cooled to below 30°C. The pH was adjusted to 6.9-7.1 with 1 N NaOH or 1N HCl after addition of the enzyme (1.5 ml enzyme/500 ml).

150 of this mixture was weighed out in each beaker. The beakers were placed in the Launder-O-Meter, and trials were run for 120 minutes.

The white fabric was rinsed thoroughly in distilled water. Fabric from different beakers was rinsed separately. The remission from the white fabric was measured on an Elrepho-photometer.

The results are shown in Fig. 1. It appears from Fig. 1 that backstaining is dependent on the concentration of Ca^{2+}. Increasing concentrations of Ca^{2+} lead to increased backstaining. Addition of EDTA results in decreased backstaining. At a molar ratio of Ca^{2+} to EDTA of 1:2-4, backstaining is at its minimum (at pH 7).

(* The endoglucanase activity is determined as the viscosity decrease of a solution of carboxymethyl cellulose (CMC) after incubation with the enzyme under the following conditions:

A substrate solution is prepared, containing 35 g/l CMC (Hercules 7 LFD) in 0.1 M tris buffer at pH 9.0. The enzyme sample to be analyzed is dissolved in the same buffer.

10 ml substrate solution and 0.5 ml enzyme solution are mixed and transferred to a viscosimeter (e.g. Haake VT 181, NV sensor, 181 rpm), thermostated at 40°C.

Viscosity readings are taken as soon as possible after mixing and again 30 minutes later. The amount of enzyme that reduces the viscosity by one half under these conditions is defined as 1 ECU).

CLAIMS

1. A process for providing improved localised variation in the colour density of the surface of dyed fabrics, the process comprising treating a dyed fabric with a cellulytic enzyme in an aqueous liquor comprising a di- or trivalent cation and a chelating agent in a molar ratio of 1:0.1-50.

2. A process according to claim 1, wherein the cellulytic enzyme is a fungal or bacterial cellulase.

3. A process according to claim 2, wherin the cellulase is an acid cellulase.

4. A process according to claim 3, wherein the acid cellulase is one derivable from a strain of Trichoderma, Irpex, Clostridium or Thermocellum.

5. A process according to claim 2, wherein the cellulase is a neutral or alkaline cellulase.

6. A process according to claim 5, wherein the cellulase is one derivable from a strain of Humicola, Fusarium, Bacillus, Cellulomonas, Pseudomonas, Myceliophthora or Phanerochaete

7. A process according to claim 3, wherein the chelating agent one which is soluble and capable of forming complexes with di- or trivalent cations at acid, neutral or alkaline pH values.

8. A process according to claim 7, wherein the chelating agent is selected from aminocarboxylic acids; hydroxyaminocarboxylic acids; hydroxycarboxylic acids; phosphates, di-phosphates, tri-polyphosphates, higher poly-phosphates, pyrophosphates; zeolites; polycarboxylic

acids; carbohydrates, including polysaccharides; hydroxypyridinones; organic compounds comprising catechol groups; organic compounds comprising hydroxymate groups; silicates; or polyhydroxysulfonates.

9. A process according to claim 8, wherein the chelating agent is an aminocarboxylic acid selected from EDTA (ethylene diamine tetra-acetic acid), DTPA (diethylene triamine pentaacetic acid), NTA (nitrilo triacetic acid), CDTA (trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid), EGTA (ethyleneglycol-O,O'-bis(2-aminoethyl)-N,N,N',N'-tetraacetic acid), or TTHA (triethylenetetraamine-N,N,N',N'-hexaacetic acid).

10. A process according to claim 8, wherein the chelating agent is a hydroxyaminocarboxylic acid selected from HEDTA (hydroxyethylene diamine triacetic acid), DEG/DHEG (dihydroxyethyl glycine), or HEIDA (N-(2-hydroxyethyl)-iminodiacetat).

11. A process according to claim 8, wherein the chelating agent is a hydroxycarboxylic acid selected from gluconic acid, citric acid, tartaric acid, oxalic acid, diglycolic acid, or glucoheptonate.

12. A process according to claim 8, wherein the chelating agent is a polyamino- or polyhydroxy-phosphonate or -polyphosphonate selected from PBTC (phosphonobutantriacetat), ATMP (aminotri(methylenphosphonic acid)), DTPMP (diethylene triaminpenta(methylenphosphonic acid), EDTMP ethylene diamintetra(methylenphophonic acid)), HDTMP (hydroxyethyl-ethylendiamintri(methylenphosphonic acid)), HEDP (hydroxyethane diphosphonic acid), or HMDTMP (hexamethylen-diamine tetra(methylene phosphonic acid)).

13. A process according to claim 8, wherein the chelating

agent is a polycarboxylic acid (or a mixture of polycarboxylic acids), selected from water soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acxid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalonic acid; carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentanetetracarboxylate, phloroglucinol trisulfonate; polyacetal carboxylates.

14. A process according to claim 13, wherein the polycarboxylic acid is selected from polyacrylate, polymaleate, maleic-methylvinylether-copolymers, maleic-acrylic-copolymers, maleic-olefine-copolymers, polyvinylpyrrolidone, polyoxymethylcarboxylates, poly(ó-hydroxy-acrylate), poly[(3-hydroxymethyl)-hexamethylene-1,3,5-tricarboxyl], poly[(3-oxymethyl)-hexamethylene-1,3,5-tricarboxyl], poly-[(4-methoxy)-tetramethylene-1,2-dicarboxylate], poly-(tetramethylene-1,2-dicarboxylate), poly(vinyl methyl ether-maleic anhydride), MW 20.000-80.000, carboxymethyloxymalonate, carboxymethyloxysuccinate, or 1,2,3,4-Cyclopentane-tetracarboxylic acid.

15. A process according to any of claims 1-14, wherein the liquor additionally comprises a buffer.

16. A process according to claim 15, wherein the buffer is a phosphate, borate, citrate, acetate, adipate, triethanolamine, monoethanolamine, diethanolamine, carbonate (especially alkali metal or alkaline earth metal, in particular sodium or potassium carbonate, or ammonium and HCl salts), diamine, especially diaminoethane, imidazole, or amino acid buffer.

17. A process according to any of claims 1-16, wherein the liquor additionally comprises a dispersing agent.

18. A process according to claim 17, wherein the dispersing agent is selected from nonionic, anionic, cationic, ampholytic or zwitterionic surfactants.

19. A process according to claim 18, wherein the dispersing agent is selected from carboxymethylcellulose, hydroxypropylcellulose, alkyl aryl sulphonates, long-chain alcohol sulphates (primary and secondary alkyl sulphates), sulphonated olefins, sulphated monoglycerides, sulphated ethers, sulphosuccinates, sulphonated methyl ethers, alkane sulphonates, phosphate esters, alkyl isethionates, acyl sarcosides, alkyl taurides, fluorosurfactants, fatty alcohol and alkylphenol condensates, fatty acid condensates, condensates of ethylene oxide with an amine, condensates of ethylene oxide with an amide, block polymers (poly ethylene glycol, polypropylene glycol, ethylene diamine condensed with ethylene or propylene oxide), sucrose esters, sorbitan esters, alkyloamides, fatty amine oxides, ethoxylated monoamines, ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof.

20. A process according to any of claims 1-19, wherein the fabric is a cellulosic fabric.

21. A process according to claim 20, wherein the fabric is denim.

22. A process according to claim 20, wherein the fabric is dyed with a vat dye, direct dye, sulphur dye or reactive dye.

23. A process according to claim 1, wherein the molar ratio of di- or trivalent cation to chelating agent is 1:0.1-10, in particular 1:0.2-5.

24. A process for providing improved localised variation

in the colour density of the surface of dyed fabrics, the process comprising treating a dyed fabric with a cellulytic enzyme in an aqueous liquor comprising less than 20 mg/l of Ca^{2+} and Mg^{2+}.

25. A process according to claim 24, wherein the cellulytic enzyme is a fungal cellulase.

26. A process according to claim 25, wherein the cellulase is an acid cellulase.

27. A process according to claim 26, wherein the acid cellulase is one derivable from a strain of _Trichoderma, Irpex, Clostridium_ or _Thermocellum_.

28. A process according to claim 25, wherein the cellulase is a neutral or alkaline cellulase.

29. A process according to claim 28, wherein the cellulase is one derivable from a strain of _Humicola, Fusarium, Bacillus, Cellulomonas, Pseudomonas, Myceliophthora_ or _Phanerochaete_ sp.

30. A process according to any of claims 24-29, wherein the liquor additionally comprises a buffer.

31. A process according to claim 30, wherein the buffer is a phosphate, borate, citrate, acetate, adipate, triethanolamine, monoethanolamine, diethanolamine, carbonate (especially alkali metal or alkaline earth metal, in particular sodium or potassium carbonate, or ammonium and HCl salts), diamine, especially diaminoethane, imidazole, or amino acid buffer.

32. A process according to any of claims 24-31, wherein the liquor additionally comprises a dispersing agent.

33. A process according to claim 32, wherein the dispersing agent is selected from nonionic, anionic, cationic, ampholytic or zwitterionic surfactants.

34. A process according to claim 33, wherein the dispersing agent is selected from carboxymethylcellulose, hydroxypropylcellulose, alkyl aryl sulphonates, long-chain alcohol sulphates (primary and secondary alkyl sulphates), sulphonated olefins, sulphated monoglycerides, sulphated ethers, sulphosuccinates, sulphonated methyl ethers, alkane sulphonates, phosphate esters, alkyl isethionates, acyl sarcosides, alkyl taurides, fluorosurfactants, fatty alcohol and alkylphenol condensates, fatty acid condensates, condensates of ethylene oxide with an amine, condensates of ethylene oxide with an amide, block polymers (poly ethylene glycol, polypropylene glycol, ethylene diamine condensed with ethylene or propylene oxide), sucrose esters, sorbitan esters, alkyloamides, fatty amine oxides, ethoxylated monoamines, ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof.

35. A process according to any of claims 24-34, wherein the fabric is a cellulosic fabric.

36. A process according to claim 35, wherein the fabric is denim.

37. A process according to claim 35, wherein the fabric is dyed with a vat dye, direct dye, sulphur dye or reactive dye.

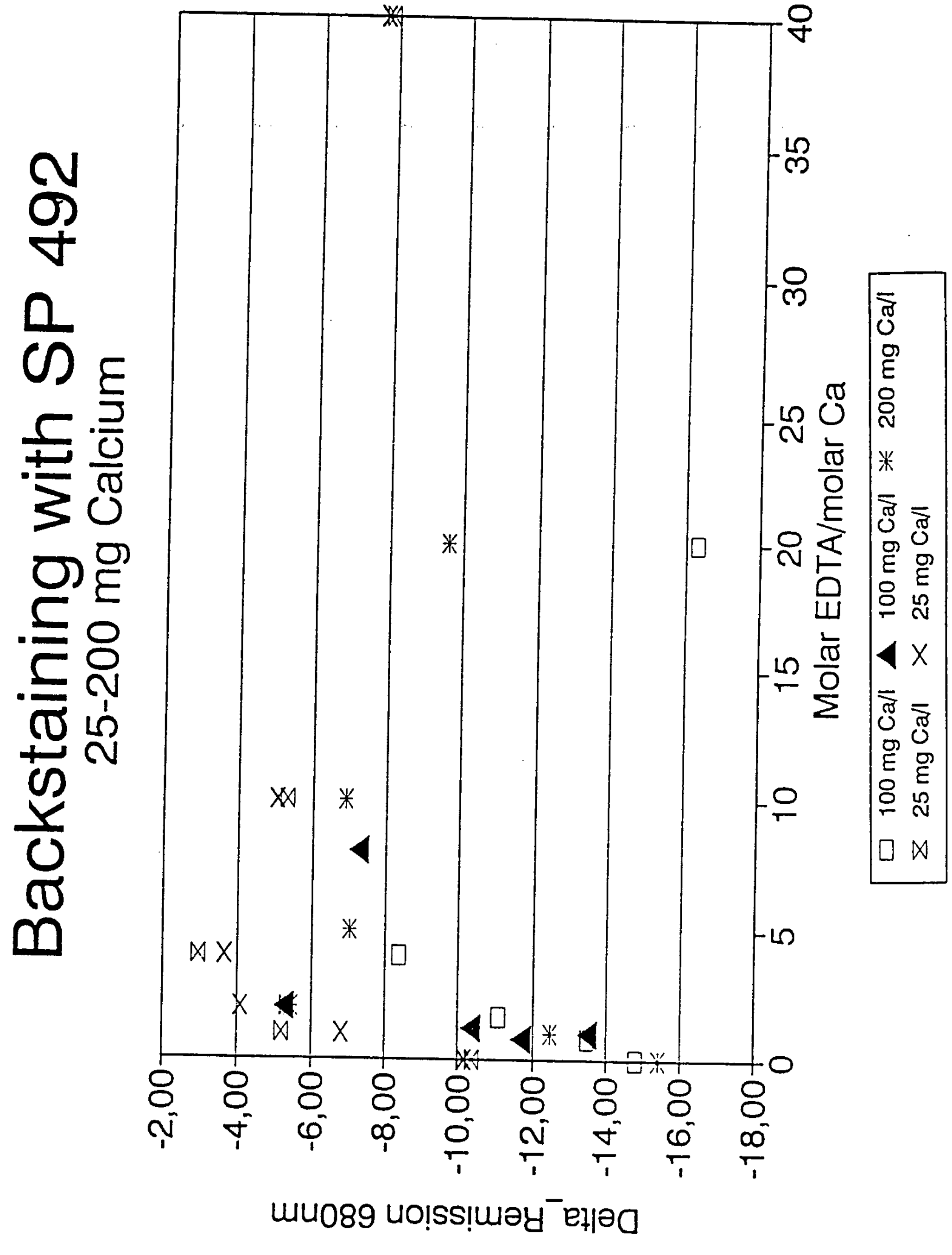
Backstaining with SP 492
25-200 mg Calcium
Delta_Remission 680nm
-2,00
-4,00
-6,00
-8,00
-10,00
-12,00
-14,00
-16,00
-18,00
0
5
10
15
20
25
30
35
40
Molar EDTA/molar Ca
□ 100 mg Ca/l
▲ 100 mg Ca/l
✳ 200 mg Ca/l
⋈ 25 mg Ca/l
× 25 mg Ca/l

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 94/00078

A. CLASSIFICATION OF SUBJECT MATTER

IPC : D06P 5/00, C12N 9/42
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : D06P, C12N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, WPAT, USPM, DIALINDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4912056 (LYNNE A. OLSON), 27 March 1990 (27.03.90), see claims -- --------	1-37

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Carolina Gomez Lagerlöf Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

07/05/94

International application No.
PCT/DK 94/00078

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4912056	27/03/90	AU-A- 2021588	16/03/89
		CA-A- 1271301	10/07/90
		EP-A- 0307564	22/03/89