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(54) Title: A PROCESS FOR THE PREPARATION OF A SYNTHETIC TANNING AGENT

(57) Abstract: A process for the preparation of a synthetic tanning agent is disclosed whereby multi functional polymer is polymerized with sulfonated aromatic compound, pretreated with organic ligand to form an organo-polymeric matrix, free from formaldehyde. The product has potential application in leather industry for not only ensuring an eco-friendly approach in chrome tanning by way of eliminating the conventional pickling process and the resulting problem of total dissolved solids (TDS) associated with the effluent, but also suggesting an exhaust aid for chrome because of its multiple carboxyl groups. The product can also be used as a retanning agent in leather processing.

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A PROCESS FOR THE PREPARATION OF A SYNTHETIC TANNING AGENT

Technical Filed

The present invention relates to a process for the preparation of a synthetic tanning agent. More particularly the present invention provides a process for the preparation of a organo-polymeric substance, which is free from formaldehyde, using for tanning leather. This polymeric substance has enormous potential application as pretanning as well as retanning agent in leather processing industry.

Background Art

Synthetic tanning agents are conventionally prepared by the condensation of naphthalene/phenol sulphonic acid or urea with formaldehyde as reported by Sharphouse (Leather Technicians Handbook, Vernon Lock Ltd., London, 1983).

As reported by Stille and Campbell (High Polymer, 27, 14, 1972), the phenol-formaldehyde condensed product, which is essentially a low molecular weight resinous material, has always a possibility of eliminating unreacted phenol or formaldehyde, thereby posing a risk of adding to toxicity.

Denzinger *et al* (U.S. Patent 5,425,784, 1995) have prepared water-soluble graft polymers of monosaccharides, oligosaccharides, polysaccharides and derivatives with crotonic acid, maleic acid, maleic anhydride, fumaric acid, citraconic acid, citraconic anhydride, C₁-C₈-alkyl- and hydroxyalkyl esters of acrylic acid, methacrylic acid or crotonic acid, mono- and di- C₁-C₈-alkyl and -hydroxyalkyl esters of maleic acid, fumaric acid and citraconic acid, acrylamide, methacrylamide, methacrolein, acrylamido-methylpropanesulfonic acid, N-vinylimidazole and mixtures, and used as a tanning agent for the self-tanning, pretanning, simultaneous tanning and retanning of pelts and skins. But these polymers do not produce leathers having fine grain, good fullness, affordable heat stability and uniform colour.

Wehling *et al* (U.S. Patent 5,340,365, 1994) have used naphthalene sulphonic acid condensate in the production of chrome leathers. They have reported that this condensation product can be used for pretreatment of delimed and bated pelts. Even though the properties of the chrome tanned leathers do not differ from those of conventionally chrome tanned, the condensed product was prepared using formaldehyde, which on ageing may undergo photo oxidation and release formaldehyde which may pose occupational hazards (Suspected carcinogens: A sub list of the National Institute for Occupational Safety and Health (NIOSH) substances list, 2nd ed. Washington DC: US

Dept of Health, Education and Welfare NIOSH, 1976.). Moreover the developed chrome 5 tanning method is associated with release of chromium in the effluent beyond the stipulated limit (2 ppm as Cr) as reported by Buljan (World Leather, November, 65, 1996). Thus it is observed that even though the phenols and phenolic acid resins based on formaldehyde condensation have exhibited freedom of choice with respect to degree of 10 cross linking, molecular weight, particle size etc, the main limitations of using these polymeric condensates are the following.

- a) They considerably lighten the color and when the amount used is too large, it will lead to a rubber-like handle of the leather.
- b) The tanned leathers undergo photo oxidation due to the presence of active methylene bridge.
- c) Slow release of formaldehyde from the tanned leathers on ageing may pose hazardous environment.

Current chrome tanning method poses severe problems due to its associated environmental problems. Industry has taken great pains to improve the chromium exhaustion. Prentiss and Sigafos (Journal of American Leather Chemists Association, 70, 481, 1975) have reported that the use of poly acrylic and poly methacrylic acids in chrome tanning improves the chrome exhaustion. Lakshminarayana *et al* (Journal of the American Leather Chemists Association, 85, 425, 1990) recommends an acrylic acid based syntan as retanning agent for chrome tanned leathers, which is prepared by the graft co-polymerization of acrylic ester and methacrylic acid onto a mixture of sulfated fish oil and alginic acid using free radical polymerization. But the major limitation associated with this product is that it leads to poor light fastness and heat resistance. Moreover, the acrylic syntans, which are generally attached to the protein through weak linkage, result in either low exhaustion in processing bath or more leaching out during subsequent wet operations. Christner *et al* (U.S. patent No 4,961,750, 1990) have reported the preparation of thio containing chromium poly acrylate tanning agents by complexing the chromium ion and an acrylate polymer together with a heterocycle containing nitrogen, oxygen, or sulfur atom, having a molecular weight between 200 and 30,000, which can be offered to pickled skins or hides. The main disadvantage in this tanning agent is the slow release of oxides of sulphur, which is carcinogenic.

The above limitations have prompted the researchers to explore possibilities of incorporating metal ion onto a polymeric matrix to form a complex for using as tanning

salt. Keeping in mind the toxic hazards caused by formaldehyde, attempts have been made to prepare synthetic tanning agent, which is free from formaldehyde, as reported by Suresh *et al* (Journal of Cleaner Production, 9, 483, 2001) and Thanikaivelan *et al* (Journal of American Leather Chemists Association, 97, 127, 2002), who have also demonstrated the use of a synthetic tanning agent based on complexation of chromium with acrylic polymer and sulfonated aromatic condensates in the presence of organic ligands for self-tanning of delimed pelts and retanning applications. The use of this product result in improved exhaustion of chromium when applied on delimed pelts and hence reduces the total dissolved solids in the effluent. The major limiting feature here is that the preparation of the syntan involves employing chromium salt for complexation, thereby giving rise to the problem of toxicity associated with chrome.

Objects of the invention

The main objective of the present invention is to provide a process for the preparation of a synthetic tanning agent, which obviates the drawbacks as detailed above.

Another objective of the present invention is to prepare a chromium exhaust aid, which can be offered to delimed pelts along with commercial BCS thus avoiding pickling process thereby reducing the total dissolved solids in the effluent.

Still another objective of the present invention is to prepare a formaldehyde free polymeric network, which helps in preventing the precipitation of chromium at lower pH values.

Yet another objective of the present invention is to prepare a polymeric product, which can be used as a retanning agent and provides leathers with improved fullness, grain firmness with uniform dyeing.

Description of the invention

Accordingly, the present invention provides a process for the preparation of synthetic organo-polymeric tanning agent essentially free from formaldehyde used for tanning leather, said process comprising the steps of:

- (a) reacting an aromatic compound with sulfuric acid at temperature in the range of 40 to 60°C to obtain sulfonized aromatic compound;
- (b) adding one or more organic ligands to the sulfonized aromatic compound obtained in step (a) and heating the mixture at temperature in the range of 60 to 80° C; 10
- (c) adding one or more multi-functional polymers to the mixture of step (b) and heating the same at temperature in the range of 40 to 100° C to obtain a reaction mixture;

- (d) adding water to the reaction mixture of step (c) and adjusting the pH value of the same in the range of 3.0 to 3.5; and
- (e) optionally, aerating the reaction mixture and drying the reaction mixture of step (d) to obtain the synthetic organo-polymeric tanning agent.

In an embodiment of the present invention wherein in step (a), the aromatic compound 20 used contains 1-14 carbon atoms.

In another embodiment of the present invention wherein in step (a), the aromatic compound is reacted with sulfuric acid for a time period in the range of 50 to 250 minutes.

In yet another embodiment of the present invention wherein in step (a), 1 to 5 moles of sulfuric acid is used per mole of aromatic compound.

In still another embodiment of the present invention wherein in step (a), the aromatic compound used is selected from the group consisting of naphthene, anthracene, or phenol.

In one more embodiment of the present invention wherein in step (b), the organic ligand used is selected from the group consisting of formic acid, citric acid, phthalic acid, salicylic acid, oxalic acid or their sodium salts either individually or in combination.

In one another embodiment of the present invention wherein in step (b), 0.01 to 0. mole of organic ligand is used per mole of the aromatic compound.

In a further embodiment of the present invention wherein in step (c), the multi-functional polymer is selected from the group consisting of polyacrylic acid, methacrylic acid or mixture thereof.

In an embodiment of the present invention wherein in step (c), 0.001 to 0.01 mole of multi-functional polymer is used per mole of the aromatic compound.

In another embodiment of the present invention wherein in step (d), 5 to 25 moles of 10 water per mole of aromatic compound is added to the reaction mixture.

In yet another embodiment of the present invention wherein in step (d), the pH of the reaction mixture is adjusted by adding sodium bicarbonate or by sodium hydroxide solution.

In still another embodiment of the present invention wherein in step (e), the reaction mixture is aerated by passing air /inert gas through the same.

In one more embodiment of the present invention wherein in step (e), the reaction mixture is aerated for the time period in the range of 30 to 60 minute.

In one another embodiment of the present invention wherein in step (e), the reaction mixture is dried either by drum drying or by spray drying.

In a further embodiment of the present invention wherein in step (e), the reaction mixture is dried at temperature in the range of 130 to 260°C.

In a further more embodiment of the present invention wherein the synthetic organo-polymeric tanning agent thus obtained has chromium exhaust in the range of 90 to 99 %.

The process of the present invention is described below in detail.

An aromatic compound having up to 14 carbon atoms is sulfonated by known method using 1 - 5 moles sulfuric acid per mole of aromatic compound for a period of not less than 90 min at a temperature in the range of 40 - 160°C. The temperature of the reaction mass is then adjusted in the range of 60 - 80°C and an aqueous mixture of 0.01 - 0.1 mole of organic ligand per mole of aromatic compound is added to the said mass. 0.0001 - 0.01 mole of multi functional polymer per mole of aromatic compound is then added to the said reaction mixture. Heating is allowed to continue for a period not less than 60 minutes at a temperature in the range of 60 - 80°C, pH of the resulting mixture is then adjusted at a range of 3.0 - 3.5 by known method to obtain the synthetic tanning agent in slurry form.

The above slurry is subjected, as optional step, to aeration for a period of 30-60 minutes followed by conventional drying at a temperature in the range of 130 - 260°C to obtain the synthetic tanning agent in powder form.

The novelty and non-obviousness of the present invention lies in polymerizing the multi functional polymer with sulfonated aromatic compound, pretreated with organic ligand, thereby forming an organo-polymeric matrix, free from formaldehyde, having potential application in leather industry for not only ensuring an eco-friendly approach in chrome tanning by way of eliminating the conventional pickling process and the resulting problem of total dissolved solids (TDS) associated with the effluent, but also suggesting an exhaust aid for chrome because of its multiple carboxyl groups, thereby ensuring an economical eco-benign approach for leather tanning.

The invention is described in detail in the following examples, which are provided by way of illustrations only and therefore should not be construed to limit the scope of the present invention.

Example 1

500 gms of naphthalene and 771 ml of concentrated sulfuric acid were taken into a 2 litre round bottom flask fitted with a stirrer. The contents of the flask were heated for 180 minutes at 40°C with constant stirring. A drop of the resulting mass was taken in a beaker and 2 ml of water was added to the beaker with shaking. A clear solution, without free

naphthalene smell was obtained. This confirms the completion of sulfonation. The sulfonated mass was transferred to a reactor fitted with a thermometer, stirrer and a dropping funnel. The mass was stirred continuously for a period of 10 min while maintaining the temperature at 60°C. A mixture of 14 gms sodium citrate, 17 gms phthalic acid, 11 gms sodium formate in 70 ml of water was added to the above sulfonated mass and stirring was continued at 60°C.

40 gms of polyacrylic acid was added to the sulphonic acid mixture and the mixture was heated to 80°C for 1 hour. A small portion of the reaction mixture was taken in a beaker and 2 ml water was added to the mass. The pH of the solution in the beaker was adjusted to 3.5 and a clear solution was obtained indicating the completion of the reaction. About 1400 ml of water was added to the mass and transferred to a bucket after cooling the reaction mass to room temperature. The pH of the mass was raised to 3.5 by adding a solution of 140 gms of sodium hydroxide in 350 ml water, followed by the addition of an aqueous solution of 350gms of sodium bicarbonate in 700 ml water. The slurry was filtered using a cloth of pore size 5-10u. The filtrate was drum dried at 130°C and the white powder was stored in a plastic container.

The product was offered to delimed goatskins at an offer of 1.5% along with 5% BCS at a float of 20%. The drum was run for 1 hr and 80% water was added. Running was continued for another hr and the penetration was assessed by checking uniform blue color along the cut section. The pH of the solution and the cut section was found to be 4.2. The bath was drained and the wet blue leathers were piled. Next day the leathers were post tanned using a conventional upper leather-processing recipe. The chromium exhaustion of the spent tan liquor was found to be 94%. The fullness of the crust leathers was found to be superior to that of conventional chrome tanned leathers.

Example 2

534 gms of anthracene and 326 ml of concentrated sulfuric acid were taken in a 2 litre round bottom flask fitted with a stirrer. The contents of the flask were heated to 140°C for 90 minutes with continuous stirring, ml of the mass was taken in a beaker and 3 ml water was added with shaking. It was observed to form a clear solution without free naphthalene smell, confirming the completion of sulfonation. The sulfonated mass was transferred to a reactor fitted with a thermometer, stirrer and a dropping funnel. The mass was stirred continuously for a period of 10 min. while maintaining the temperature at 80°C. A mixture of 5.4 gms oxalic acid, 4.14 gms salicylic acid and 10 gms phthalic acid dissolved in 50 ml water was added to the above sulfonated mass and stirring was continued at 80°C.

1.5 gms of poly methacrylic acid was added to the sulphonic acid mixture and the mixture was heated to 80°C for 1 hour. A small portion of the reaction mixture was taken in a beaker and 2 ml water was added to the mass. The pH of the solution in the beaker was adjusted to 3 and a clear solution was obtained indicating the completion of the 30 reaction. About 540 ml of water was added to the mass and transferred to a bucket after cooling the reaction mass to room temperature. The pH of the mass was raised to 3 by adding a solution of 220 gms of sodium hydroxide in 500ml water, followed by the addition of an aqueous solution of 200 gms of sodium carbonate in 400ml water. The slurry was aerated for 45 minutes conventionally and filtered using a cloth of pore size 5-10 μ . The filtrate was spray dried at 260°C and the white powder was stored in a plastic container.

The prepared syntan was added to the delimed sheepskins at an offer of 1.0% along with 5% BCS at a float of 20%. The drum was run for 1 hr and 80% water was added. Running was continued for another hr and the penetration was assessed by checking uniform blue color along the cut section. The pH of the solution and the cut section was 10 found to be 4.4. The bath was drained and the wet blue leathers were piled. Next day the leathers were post tanned using a conventional garment leather processing recipe. The chromium exhaustion of the spent tan liquor was found to be 95%. The fullness of the crust leathers was found to be superior to that of conventional chrome tanned leathers.

Example 3

94 gms of phenol and 54 ml of concentrated sulfuric acid were taken in a 250 ml round bottom flask fitted with a stirrer. The contents of the flask were heated to 80°C for 100 minutes with continuous stirring. 1 ml of the resulting mass was taken in a beaker and 3 ml water was added. On shaking, a clear solution was obtained confirming the completion of sulfonation. The sulfonated mass was transferred to a reactor fitted with a 20 thermometer, stirrer and a dropping funnel. The mass was stirred continuously for a period of 10 min while maintaining the temperature at 80°C. A mixture of 1.1 gm citric acid, 0.28 gm salicylic acid and 0.56 gms sodium phthalate dissolved in 10 ml of water was added to the above sulfonated mass and stirring was continued at 70°C.

20 gms of polyacrylic acid was added to the sulphonic acid mixture and the mixture was heated to 70°C for 1 hour. A small portion of the reaction mixture was taken in a beaker and 2 ml water was added to the mass. The pH of the solution in the beaker was adjusted to 3.5 and a clear solution was obtained indicating the completion of the reaction. About

90 ml of water was added to the mass and, transferred to a bucket after cooling the reaction mass to room temperature. The pH of the mass was raised to 3.5 by adding a solution of 40 gms of sodium carbonate dissolved in 100 ml water, followed by the addition of a solution of 20 gms sodium bicarbonate dissolved in 50 ml water. The slurry was filtered using a cloth of pore size 5-10u. The filtrate was spray dried at 260°C and the white powder was stored in a plastic container.

The product was offered to delimed cow sides at an offer of 1.5% along with 8% BCS at a float of 20%. The drum was run for 2 hrs and 80% water was added. Running was continued for another 4 hrs and the penetration was assessed by checking uniform blue color along the cut section. The pH of the solution and the cut section was found to be 4.0. The bath was drained and the wet blue leathers were piled. Next day the leathers were post tanned using a conventional upper leather processing recipe. The chromium exhaustion of the spent tan liquor was found to be 92%. The fullness of the crust leathers was found to be superior to that of conventional chrome tanned leathers.

Example 4

256 gms of naphthalene and 544 ml of concentrated sulfuric acid were taken in a 2 litre round bottom flask fitted with a stirrer. The contents of the flask were heated to 160°C for 90 minutes. 1 ml of the resulting mass was taken in a beaker and 2ml water was added to the mass with shaking. It was observed that the solution was clear indicating the completion of sulfonation. The sulfonated mass was transferred to a reactor fitted with a thermometer, stirrer and a dropping funnel. The mass was stirred continuously for a period of 10 min. while maintaining the temperature at 80°C. A mixture of 8.4 gms citric acid, 16.6 gms phthalic acid and 4 gms sodium formate dissolved in 50 ml water was added to the above sulfonated mass and stirring was continued at 80°C.

A mixture of 20 gms poly methacrylic acid and 5 gms polyacrylic acid was added to the sulphonic acid mixture and the mixture was heated to 60°C for 1 hour. A small portion of the reaction mixture was taken in a beaker and 2 ml water was added to the mass. The pH of the solution in the beaker was adjusted to 3.5 and a clear solution was obtained indicating the completion of the reaction. About 900 ml of water was added to the mass and is transferred to a bucket after cooling the reaction mass to room temperature. The pH of the mass was raised to 3.5 by adding a solution of 100 gms of sodium hydroxide dissolved in 200 ml water, followed by the addition of a solution of 300 gms sodium bicarbonate dissolved in 600 ml water. The slurry was filtered using a cloth of pore size 5-

10 μ . The filtrate was drum dried at 130°C and the white powder was stored in a plastic container.

The product was offered to delimed buff calfs at an offer of 1.5% along with 8% BCS at a float of 20%. The drum was run for 2 hrs and 80% water was added. Running was continued for another 4 hrs and the penetration was assessed by checking uniform blue color along the cut section. The pH of the solution and the cut section was found to be 4.0. The bath was drained and the wet blue leathers were piled. Next day the leathers were post tanned using a conventional upper leather-processing recipe. The chromium exhaustion of the spent tan liquor was found to be 94%. The fullness of the crust leathers was found to be superior to that of conventional chrome tanned leathers.

The following are the advantages of the present invention:

1. The process is very simple and does not require any complicated and critical control measures.
2. Cheaper and indigenously available starting materials are used for the preparation of the polymeric syntan ensuring its cost effectiveness.
3. The process results in a polymer which is free from the hazardous elements like formaldehyde and chromium.
4. The polymeric product is freely soluble in water and hence can be offered along with basic chromium sulfate on delimed pelts.
5. The process ensures no precipitation of chromium when it is offered on delimed pelts at a pH in the range of 8 - 8.5.
6. The process ensures high uptake of chromium when compared to normal wet blue process.
7. The polymer is incorporated with aromatic sulphonic acids to impart fullness to the tanned leathers.
8. This syntan enhances the chrome up take and no release of formaldehyde in the tan liquor ensuring an eco-friendly and economically viable tanning process.
9. The product produces wet blue leathers with required fullness apart from serving as chrome exhaust aid.
10. The product can be used a co-tanning agent along with BCS and as a retanning agent.
11. The shelf life of the product is about 5-2 years.
12. The tanned leathers do not undergo photo oxidation since it does not contain any active methylene groups in the system unlike in other condensed tanning agents.

Claims:

- 1) A Process for the preparation of synthetic organo-polymeric tanning agent essentially free from formaldehyde used for tanning leather, said process comprising the steps of:
 - a) reacting an aromatic compound with sulfuric acid at temperature in the range of 40 to 60°C to obtain sulfonized aromatic compound;
 - b) adding one or more organic ligands to the sulfonized aromatic compound obtained in step (a) and heating the mixture at temperature in the range of 60 to 80° C;
 - c) adding one or more multi-functional polymers to the mixture of step (b) and heating the same at temperature in the range of 40 to 100° C to obtain a reaction mixture;
 - d) adding water to the reaction mixture of step (c) and adjusting the pH value of the same in the range of 3.0 to 3.5; and
 - e) optionally, aerating the reaction mixture and drying the reaction mixture of step (d) to obtain the synthetic organo-polymeric tanning agent.
- 2) A process as claimed in claim 1 herein in step (a), the aromatic compound used contains 1-14 carbon atoms.
- 3) A process as claimed in claim 1 wherein in step (a), the aromatic compound reacted with sulfuric acid for a time period in the range of 50 to 250 minutes.
- 4) A process as claimed in claim 1 wherein in step (a), 5 moles of sulfuric acid is used per mole of aromatic compound.
- 5) A process as claimed in claim 1 wherein in step (a), the aromatic compound used is selected from the group consisting of naphthene, anthracene, or phenol.
- 6) A process as claimed in claim 1 wherein in step (b), the organic ligand used is selected from the group consisting of formic acid, citric acid, phthalic acid, salicylic acid, oxalic acid or their sodium salts either individually or in combination.
- 7) A process as claimed in claim 1 wherein in step (b), 0.01 to 0. mole of organic ligand is used per mole of the aromatic compound.
- 8) A process as claimed in claim 1 wherein in step (c), the multi-functional polymer is selected from the group consisting of polyacrylic acid, methacrylic acid or mixture thereof.

- 9) A process as claimed in claim 1 wherein in step (c), 0.001 to 0.01 mole of multi-functional polymer is used per mole of the aromatic compound.
- 10) A process as claimed in claim 1 wherein in step (d), 5 to 25 moles of water per mole of aromatic compound is added to the reaction mixture.
- 11) A process as claimed in claim 1 wherein in step (d), the pH of the reaction mixture is adjusted by adding sodium bicarbonate or by sodium hydroxide solution.
- 12) A process as claimed in claim 1 wherein in step (e), the reaction mixture is aerated by passing air /inert gas through the same.
- 13) A process as claimed in claim 1 wherein in step (e), the reaction mixture is aerated for the time period in the range of 30 to 60 minute.
- 14) A process as claimed in claim 1 wherein in step (e), the reaction mixture is dried either by drum drying or by spray drying.
- 15) A process as claimed in claim 1 wherein in step (e), the reaction mixture is dried at temperature in the range of 130 to 260°C.
- 16) A process as claimed in claim 1, wherein the synthetic organo-polymeric tanning agent thus obtained has chromium exhaust in the range of 90 to 99 %.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 03/03592

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C14C3/20 C14C3/22

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 7 C14C

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 26789 A (PEACH STATE LABS INC) 24 November 1994 (1994-11-24) example 1 page 4, line 13 -page 6, line 11 ---	1-16
A	US 5 340 365 A (WEHLING BERNHARD ET AL) 23 August 1994 (1994-08-23) cited in the application column 2, line 3 - line 56 column 3, line 54 -column 4, line 2; example 1 ---	1-16
A	EP 0 428 481 A (CIBA GEIGY AG) 22 May 1991 (1991-05-22) page 3, column 4; examples 2,3 ---	1-16
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- *Z* document member of the same patent family

Date of the actual completion of the international search

21 January 2004

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 03/03592

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>THANIKAIVELAN P ET AL: "A NOVEL FORMALDEHYDE-FREE SYNTHETIC CHROME TANNING AGENT FOR PICKLE-LESS CHROME TANNING: COMPARATIVE STUDY ON SYNTAN VERSUS MODIFIED BASIC CHROMIUM SULFATE" JOURNAL OF THE SOCIETY OF LEATHER TECHNOLOGIES AND CHEMISTS, NORTHAMPTON, GB, vol. 97, 2002, pages 127-136, XP009012586 cited in the application the whole document -----</p>	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/IB 03/03592

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