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(54) PROCESS FOR PREPARING A SYNTHETIC ALUMINIUM TANNING AGENT

VERFAHREN ZUR HERSTELLUNG EINES SYNTHETISCHEN ALUMINIUMGERBMITTELS

PROCÉDÉ DE PRÉPARATION D'UN AGENT DE TANNAGE EN ALUMINIUM DE SYNTHÈSE

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Description

[0001] The present invention relates to a process for the preparation of a novel synthetic aluminium tanning agent. More particularly the present invention provides a process for the preparation of a synthetic organo-aluminium tanning agent without using formaldehyde, which forms an alternative to chrome tanning material. The compound has use as a self-tanning agent for hides and skins. Additionally, it is envisaged to be capable to produce fuller leathers with adequate shrinkage temperature for producing leathers with desirable properties. It is also envisaged that the white base of the leathers enhances dyeability and acts as dye saver apart from ample production of white leathers.

[0002] Conventionally skins/hides are stabilised against microbial degradation by tanning. Chrome tanning has been the most predominant method of tannage for the commercial purpose. The major limitation associated with this is that the chrome tanned leathers are empty in nature and hence need heavy retanning for its final performance. Unlike chamois leather, which is essentially of oil tanned, chrome tanned leather does not provide any lubrication among the fibres. Hence strong fatliquoring becomes mandatory for the desired level of softness.

[0003] Conventional chrome tanning practices employ basic chromium sulphate salt, a progenitor of several chromium species, having various charges and degree of polymerisation. The kinetic inertness of certain chromium species lends itself to poor exhaustion (50-70%) of chrome tanning salt. Thus the commercial chrome tanning activities release chromium in the range of 2000-5000 ppm.

[0004] Bellavere et al (Environmental Technology Letters, 2, 119, 1981), report that the environmental consequences arising from discharge of industrial wastewater containing chromium into water bodies are enormous. Tsou et al (Chemical Research in Toxicology, 10, 962, 1997) have proved that chromium has the ability to cause cancer, Blankenship et al (Toxicology and Applied Pharmacology, 126, 75, 1994) have reported even cell death as ultimate result due to the influence of chromium. Wide ecological concern as well as economic loss has compelled researchers to look for suitable alternatives to chromium.

[0005] Several methods have been evolved over the years for better management of chromium in leather industry, as reported by Chandrasekaran (Leather Science, 34, 91, 1987). Among them the development of mineral alternatives to chromium have been gaining momentum.

[0006] Aluminum tanning is one of the oldest methods of tanning. An old name 'tawing' has been used for this process, which consists of treating the skin with potassium alum in the form of paste including sodium chloride, egg yolk, flour and water. Aluminum tanned leathers are sensitive to water and heat. Aluminum tanned leather

has a shrinkage temperature in the range of 75-82°C depending on the method of tanning used. Its water resistance is unsatisfactory, since even a wash with the cold water slowly removes aluminium compounds from leather. Aluminium being d^o element, its complexes are much less stable than those of chromium; and thus their binding to collagen is much weaker. This is the reason why aluminium salts are used in contemporary tanning almost exclusively in combined tannage processes. Generally aluminium tanning is done in floats of zero basicity at high concentrations in the presence of sodium chloride to prevent swelling, because the pH of the float is as low as 2.5 - 3.5. No washing is employed after tanning.

[0007] A detailed study of the masking action of organic acids on aluminium sulfate and chloride was done by Simoncini et al (Cuoio Pelli Mat. Conc. 54, 439 & 711, 1978). They have described a tanning method based on the use of aluminium complex containing citric acid or ethylenediamine tetra acetic acid as complexing agent, which gives good results. However, the process requires a pretanning and retanning with vegetable tannins and glutaraldehyde.

[0008] In a detailed study by Williams-Wynn (Journal of the Society of Leather Technologists and Chemists, 53, 64, 1969) using various ligands such as formate, acetate, lactate, tartrate and citrate, most stable leathers are obtained with formate, acetate and lactate with shrinkage temperature in the range of 74 - 78°C. If the complexing agent is too strong it will not be displaced by protein carboxyl groups and the skin will remain untanned. Similar conclusions have been drawn by Kuntzel and Rizk (Leder, 13, 101, 1962).

[0009] Mezey (PhD Thesis, Faculty of Science, Lyon, France, 1925) has studied the tanning effect of aluminum sulphate on unlimed skin at various basicities in the presence and absence of common salt. The absence of salt produces hard and horny translucent skin without leathery feel upon drying, which is due to swelling induced by absorption of sulphuric acid. The presence of a sufficient amount of common salt to repress the swelling effect produces supple and opaque leather. However, on washing it reverts to the swollen unlimed skin condition. Studies on tanning using previously adjusted basic solutions of aluminium sulphate by Chambard and Grall (Bull. assoc. franc. chimistes inds. cuir et doc. sci. et tech. ind. cuir, 10(3), 17, 28, 1948) and Mezey (PhD Thesis, Faculty of Science, Lyon, France, 1925) have proved that the tanning using various basic aluminum sulphate solutions without common salt results in hard and horny untanned skins in spite of higher absorption of tanning bath components. In the presence of salt, opaque and supple leather having better resistance to hydrolysis than the leather, which is obtained by tannage using zero basicity and shrinkage temperature being about 65 rather than 47°C.

[0010] Aluminium based tanning agents like Lutan B and ATC - 21 have not found much commercial acceptability because of the ready reversal of aluminium as alu-

minium hydroxide at pH values in the range of 5.0-6.0. Lipowski (US Patent 4,443,382, 1984) has developed an aluminium salt of aromatic sulfonic acid condensate for retanning applications. However, the polymeric matrix is made using formaldehyde. The most commercial use of aluminium in leather industry until now has been as a dye adjunct. The high cationic potential of Al(III) makes such salts useful for enhancing the color yield.

[0011] It has been reported that polyhydroxy aluminium gels aid the exhaustion of chromium during tanning and function as chrome saver by Ramasami et al (Proceedings of the 22nd LERIG, Madras, 167, 1987). However, the reversibility in binding to leathers has limited the usage of Al(III) salts as chrome saver. Alutan, an aluminium based synthetic tanning agent, has aluminium in the stabilized form and binds irreversibly to the substrate as reported by Kanthimathi et al (Leather Science, 32, 59, 1985). By using this aluminium syntan as chrome saver, the exhaustion level of chromium improves to about 90% as reported by Rao et al (Proceedings of the XXVth IULTCS congress, Chennai, 295, 1999). However, this syntan was used only as a co-tanning agent along with 4-6% chrome salt. Further, the syntan was based on formaldehyde condensates. Swarna et al (Proceedings of the XXVth IULTCS Congress, Chennai, 322, 1999) has reported about such formaldehyde condensates that the tanned leathers on aging may release free formaldehyde ranging from 1500 to 15000 ppm, which does not meet the tolerable limit of 5-10 ppm of free formaldehyde as accounted by Mark et al (Kirk Othmer Encyclopedia of Chemical Technology, Volume 13, John Wiley and Sons, New York, 3rd Edition, 1978). The tanning potency of phenol-formaldehyde condensates has been reported by Gustavson (The Chemistry of Tanning Processes, Academic press, Volume 2, p. 4, 1956). But the major disadvantages of such polymeric condensates are

- a) the tanned leathers show discoloration
- b) the sulfonic acid groups introduced in the system to give soluble matrix would competitively inhibit the binding of anionic dyes
- c) slow release of formaldehyde from the tanned leathers on aging may pose hazardous environment.

[0012] US-A-4723001 describes general background art in the field of dyeing nitrogen containing or hydroxy-containing materials. Certain chromium complexes having a radical of a bidentate bianionic compound water or an amine-type compound, a benzene or naphthalene diazo component and other groups attached to the chromium atom are described.

[0013] Derwert abstract number 1988 - 153443 (SH1348372A) describes the treatment in adrumona semi-finished cattle leather after chrome-tanning and neutralisation by treating with a water soluble antiseptic. Thereafter, dyeing and fat liquoring processes are carried out and acetic or formic acid is then added to fix the resin

into the structure of the derma followed by drying.

[0014] Further general background is described in GB-A-1554886 which discloses thrombocytes which have been reacted with a tanning agent. A suspension of thrombocytes is also disclosed.

[0015] GB-A-2069694 discloses immunological reagents for detecting rheumatoid factor. The reagent disclosed comprises a complex of red blood cells and antibodies soluble with respect to the cells and immunologically fixed thereto. The reagent is stable and capable of providing hemagglutination subject to contacting it with detectable concentrations of rheumatoid factor. The reagent may be compared by subjecting red cells and antibodies to successive treatments with aldehydes or tanning agents and with proteinic substances having dispersive properties, for example albumin.

[0016] US-A-4830632 relates to aqueous compositions from a sulfonated phenol, and amine and the tanning salt. The tanning salt is mixed with a composition containing the sulfonated phenol, and the amine and optionally a salt of EDTA or pyrophosphate.

[0017] Further background information is provided in GB-A-2068999 which relates to tanning leather. Animal skins are treated in a bath containing a polyvalent metal salt and polymer or oligomer containing carboxyl, hydroxy or carboxyl derivative functional groups capable of reacting with the polyvalent ion. The colour, or lack of it in the animal skin is stabilised by the polymer or oligomer.

[0018] The main pre-requisite for conventional chrome tanning process, carried out using either basic chromium sulphate (BCS) or high exhaust chrome tanning salt, is to pickle the pelt by employing acid and salt in aqueous medium whereby the emanated liquor is loaded with dissolved solids, chlorides and sulphates, leading thereby to the environmental pollution.

[0019] The main objective of the invention is to provide a process for the preparation of a novel synthetic aluminium tanning agent, which obviates the drawbacks stated above.

[0020] Another objective of this invention is to provide an organo aluminium complex for direct tanning of delimed pelts without the conventional pickling process thereby reducing the total dissolved solids in the effluent.

[0021] Yet another objective of the invention is to provide a method for the preparation of Al(III) tanning salt in homogenous chemical formulation in which Al(III) binds irreversibly with skin/hide matrix and resists washing even at a pH 7.

[0022] Still another objective of the invention is to provide a method for the preparation of Al(III) tanning salt which when used in tanning gives leathers with shrinkage temperature more than 80°C unlike the conventional aluminium tanned leathers.

[0023] Still another objective of the invention is to provide a product for the manufacture of white leathers through an eco-friendly application procedure.

[0024] Yet another objective of the invention is to provide a product, which serves as dye saver and efficient

chrome saver.

[0025] Still another objective of the invention is to provide aluminium based syntan, which offers soft and fuller leathers unlike the conventional chrome tanned leather.

[0026] Accordingly the present invention provides a process for the preparation of a novel synthetic aluminium tanning agent, which comprises

- i) sulfonating an aromatic compound having up to 14 carbon atoms followed by the addition of an aqueous mixture of organic ligands and polyfunctional polymer,
- ii) adding trivalent aluminium salt along with water to the reaction mixture formed in step(i) and mixing the reaction mass to form a complex,
- iii) adding sulfosalicylic acid to the reaction mixture formed in step(ii) to form a slurry,
- iv) adjusting pH of the slurry formed in step (iii), in range of 2.5-3.0 by alkalizing agent,
- v) drying the slurry to obtain the tanning agent in powder form.

[0027] In one embodiment of the invention, the sulfonation in step (i) is carried out at a temperature in the range of 25-160°C.

[0028] In yet another embodiment of the invention, the aqueous mixture of organic ligands and polyfunctional polymer is added to the sulfonated aromatic compound at a temperature in the range of 60 - 80°C.

[0029] In a further embodiment of the invention, the addition of trivalent aluminium salt along with water to the reaction mixture formed in step(i) is carried out at a temperature in the range of 60 - 80°C.

[0030] In another embodiment of the invention, the addition of sulfosalicylic acid to the reaction mixture formed in step(ii) is done at a temperature in the range of 60 - 80°C.

[0031] In yet another embodiment of the invention, the slurry obtained in step (iv) is aerated for a period of 30 - 60 min before drying at a temperature in the range of 130-260°C to get the tanning agent in powder form.

[0032] In another embodiment of the invention, the aromatic compound used is selected from the group consisting of phenol, phenolic acid, naphthol, naphthalene and anthracene.

[0033] In another embodiment of the invention, the amount of the aromatic compound used is in the range of 0.5 - 2.0 moles per mole aluminium.

[0034] In yet another embodiment of the invention, sulfonation is carried out using sulfuric acid in an amount in the range of 1 - 5 moles per mole of aluminium.

[0035] In yet another embodiment of the invention, the organic ligand used is selected from the group consisting of formic acid, citric acid, phthalic acid, poly carboxylic acid, oxalic acid, salicylic acid, sodium salts thereof and any mixture thereof.

[0036] In another embodiment of the invention, the amount of organic ligands used is in the range of 0.001

- 0.05 mole per mole of aluminium.

[0037] In yet another embodiment of the invention, the polyfunctional polymer used is selected from the group consisting of polyacrylic acid, polyacryl amide, polymethacrylic acid, and any mixture thereof.

[0038] In a further embodiment of the invention, the amount of the polyfunctional polymer used is in the range of 0.0001- 0.001 mole per mole of aluminium.

[0039] In yet another embodiment of the invention, the trivalent aluminium salt is selected from the group consisting of aluminium sulfate, aluminium chloride, aluminium ammonium sulfate and aluminium potassium sulfate.

[0040] In another embodiment of the invention, the amount of water added to the reaction mixture is in the range of 5 - 30 moles per mole of aluminium.

[0041] In yet another embodiment of the invention, the amount of sulfosalicylic acid used is in the range of 0.001- 0.01 moles per mole of aluminium.

[0042] In yet another embodiment of the invention, the amount of sulfuric acid used for sulfonating aromatic compound is in the range of 0.001 - 0.01 moles per mole of aluminium.

[0043] In another embodiment of the invention, drying of the slurry is done by drum drying or spray drying.

[0044] The process of the present invention is described below in detail.

[0045] An aromatic hydrocarbon having up to 14 carbon atoms, calculated as 0.5-2.0 moles per mole of aluminium to be used, is sulfonated by known method using 1 to 5 moles sulphuric acid per mole of aluminium for a period of not less than 60 minutes at a temperature in the range 25-160°C. An aqueous mixture of 0.001 - 0.05 mole of organic ligand per mole of aluminium is then added to the sulfonated mass along with 0.0001- 0.001 moles polyfunctional polymer per mole of aluminium at a temperature of 60 - 80°C with continuous stirring whereby the organic matrix is built up.

[0046] Trivalent aluminium salt is then added to the resulting mixture along with 5 - 30 moles of water per mole of aluminium while maintaining the temperature in the range of 60 - 80°C. Al(III) being a d⁰ non-transition element, needs a critical additive that is capable of converting it to a pseudo-transition element by transferring the electrons to 3s, 3p and 3d orbitals. Hence, the reaction is continued for a period of 60 minutes. A critical additive in the range of 0.001 - 0.01 mole per mole of aluminium is sulfonated by known method using 0.001 - 0.01 moles sulphuric acid per mole of aluminium for a period of not less than 3 hours at a temperature in the range 25 - 28°C. The sulfonated critical additive is then added to the reaction mixture. The heating and stirring was continued for another 30 min. after which the completion of the reaction is confirmed by known solubilization technique. The resulting mixture is then adjusted to a pH of 2.5 - 3.0 by conventional method. The slurry is dried conventionally at a temperature range of 130 - 260°C to obtain the organo aluminium complex as a white powder.

[0047] The novelty and non obviousness of the present

development lies in using polyfunctional polymer for providing a polymeric matrix without ethylene bridge with suitable critical additive that is capable of anchoring a d^0 non-transition element, Al(III), by charge transfer mixing of 3s, 3p and 3d orbitals. The irreversible binding of aluminium to the organic matrix is achieved by using organic ligands in combination with critical additive having ligating sites capable of anchoring trivalent aluminium ion.

[0048] The invention is described in the following examples, which are provided for illustration only and should not be construed to limit the scope of the present invention.

Example 1

[0049] 25 gms of naphthalene and 25 ml of conc. sulfuric acid were taken into a 250 ml round bottomed flask fitted with a stirrer. The contents of the flask were heated to 80°C for 120 minutes with constant stirring. A drop of the resulting mass was taken in a beaker and 1 ml water was added to the same with shaking. A clear solution without any naphthalene smell was obtained confirming the completion of sulfonation. Simultaneously, 0.5 gm salicylic acid was taken in a separate beaker and 0.5 ml concentrated sulfuric acid was added with stirring at 25°C. The slurry was left aside with occasional stirring for 3 hrs. The naphthalene sulfonic acid, prepared in flask was allowed to cool down to 60°C and 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 with the help of the thermostat. A mixture of 0.2 gm poly acrylic acid, 0.25 gm phthalic acid, 1 gm citric acid and 0.14 gm salicylic acid was dissolved in 10 ml water in a beaker and the same was added to the reaction mass in the reactor through the dropping funnel. The mixture was heated at 65°C for 20 min. 250 gms of aluminium sulfate was added to the above mass along with 100 ml of water with vigorous stirring. The temperature of the bath was gradually raised to 70°C and allowed heating to continue for another 60 min. The sulfo salicylic acid which was prepared in the beaker was added to above mass and heating was continued for another 30 minutes. The mixture was transferred to a bucket and pH was raised to 2.5 by adding 60 gms sodium sulfite dissolved in 100 ml water while continuing stirring. The air was passed through the resulting solution for a period of 70 minutes. Slurry was filtered using muslin cloth of pore size 5-10 μ . The filtrate was drum dried at 130°C and the powder stored in a plastic container.

[0050] The product was used for tanning the delimed goat skins at an offer of 1.5% as Al_2O_3 on pelt weight. The tanned leather was left over night and the shrinkage temperature was found to be 85°C exhibiting 80-82% exhaustion of aluminium.

Example 2

[0051] 70 gms of anthracene and 50 ml of conc. sulfuric acid were taken into a 500 ml round bottomed flask fitted with a stirrer. The contents of the flask were heated to 140°C for one hr. with continuous stirring. 1 ml of the resulting mass was taken in a beaker and 3 ml water was added to the same beaker with shaking. It was observed to form a clear solution, confirming the completion of sulfonation. In another beaker 0.3 gms salicylic acid was sulfonated simultaneously by adding 0.3ml conc. sulfuric acid and stirred thoroughly at 28°C. This mass was kept aside for 4 hrs with occasional stirring. The anthracene sulfonic acid was cooled to 60°C and transferred to the reactor fitted with a condenser, stirrer and a dropping funnel. The reactor was fitted into a thermostated water bath and the sulfonated mass was stirred for 10 min. at a temperature of 60°C. A mixture of 1 gm citric acid, 0.06 gm oxalic acid, 0.01 gm phthalic acid, 0.03 gm sodium formate and 0.1 gm poly acrylic acid was dissolved in 15 ml water and added to the reaction mixture keeping the temperature at 60°C. The mass was heated at 65°C for 40 minutes. 200 gms of aluminium potassium sulfate was dissolved in 150 ml water and added to the reactor while continuing the heating and stirring. The temperature was gradually raised to 75°C. The mixture was heated for one hour. The pre made sulfo salicylic acid was added to the reaction mixture and stirred for 40 min. while maintaining the above temperature. The mixture was transferred to a bucket and the pH was adjusted to 2.5 by adding aqueous slurry of 50 gms of sodium bicarbonate and stirring continued till the effervescence stopped. The mass was filtered using a muslin cloth of pore size 5-10 μ . The filtrate was spray dried at a temperature of 230°C and the powder was stored in a plastic container.

[0052] The product was used for tanning the delimed goat skins at an offer of 1.5% as Al_2O_3 on pelt weight. The tanned leather was left over night and the shrinkage temperature was found to be 84°C, exhibiting an uptake of 80% aluminium.

Example 3

[0053] 50 gms of phenol and 100 gms of concentrated sulfuric acid were taken into a 500 ml round bottomed flask fitted with a stirrer. The contents of the flask were heated to 120°C for 1 hr. with continuous stirring. 1 ml of the resulting mass was taken in a beaker and 3 ml of water was added. On shaking, a clear solution was obtained confirming the completion of sulfonation. Simultaneously, 0.04 gms of salicylic acid was sulfonated using 0.05 ml concentrated sulfuric acid at 26°C. The contents were stirred occasionally and left aside for 3 hrs. The phenol sulfonic acid prepared in the flask was allowed to cool down to 60°C and transferred to the reactor fitted with a thermostat, stirrer and a dropping funnel. The mass was stirred for 10 min. at 60°C. A mixture of 0.6 gm poly acrylic acid, 0.05 gm of phthalic acid in 2 ml water was

added to the reactor through the dropping funnel. The mixture was stirred for 30 min. maintaining the temperature at 60°C. 136 gms of ammonium aluminium sulfate was added to the above mass along with 100 ml water with vigorous stirring. The temperature of the bath was gradually raised to 70°C and heating continued for 1 hr. The pre made sulfo salicylic acid was added to the reactor and the heating was continued for 1 hour. The reaction mixture was transferred to a bucket and the pH was adjusted to 3.0 using sodium bicarbonate. The solution was filtered and dried using a spray drier at a temperature of 260°C. The dried product was packed in a plastic container.

[0054] This product was used for tanning the delimed goatskins at an offer of 1.5% as Al_2O_3 on pelt weight. The tanned leathers were aged for one day and the shrinkage temperature of the tanned leather was found to be 85°C, exhibiting 78% exhaustion of aluminium.

Example 4

[0055] 73 gms of phenolic acid and 100 gms of concentrated sulfuric acid were taken into a 500 ml round bottomed flask fitted with a stirrer. The contents of the flask were maintained at temperature of 28°C for 1 hr. with continuous stirring. 1 ml of the resulting mass was taken in a beaker and 3 ml of water was added. On shaking, a clear solution was obtained confirming the completion of sulfonation. Simultaneously, 0.04 gms of salicylic acid was sulfonated using 0.05 ml concentrated sulfuring acid at 26°C. The contents were stirred occasionally and left aside for 3 hrs. The sulfonated phenolic acid prepared in the flask was allowed to cool down to 60°C and transferred to the reactor fitted with a thermostat, stirrer and a dropping funnel. The mass was stirred for 10 min. at 60°C. A mixture of 0.6 gm poly acrylic acid, 0.05 gm of phthalic acid in 2 ml water was added to the reactor through the dropping funnel. The mixture was stirred for 30 min. maintaining the temperature at 60°C. 72 gms of aluminium chloride was added to the above mass along with 100 ml water with vigorous stirring. The temperature of the bath was gradually raised to 70°C and heating continued for 1 hr. The pre made sulfo salicylic acid was added to the reactor and the heating was continued for 1 hour. The reaction mixture was transferred to a bucket and the pH was adjusted to 3.0 using sodium bicarbonate. The solution was filtered and dried using a spray drier at a temperature of 260°C. The dried product was packed in a plastic container.

[0056] This product was used for tanning the delimed goatskins at an offer of 1.5% as Al_2O_3 on pelt weight. The tanned leathers were aged for one day and the shrinkage temperature of the tanned leather was found to be 84°C, exhibiting 78% exhaustion of aluminium.

Example 5

[0057] 76 gms of naphthol and 100 gms of concentrat-

ed sulfuric acid were taken into a 500 ml round bottomed flask fitted with a stirrer. The contents of the flask were heated to 70°C for 1 hr. with continuous stirring. 1 ml of the resulting mass was taken in a beaker and 3 ml of water was added. On shaking, a clear solution was obtained confirming the completion of sulfonation. Simultaneously, 0.04 gms of salicylic acid was sulfonated using 0.05 ml concentrated sulfuring acid at 26°C. The contents were stirred occasionally and left aside for 3 hrs. The naphthol sulfonic acid prepared in the flask was allowed to cool down to 60°C and transferred to the reactor fitted with a thermostat, stirrer and a dropping funnel. The mass was stirred for 10 min. at 60°C. A mixture of 0.6 gm poly acrylic acid, 0.05 gm of phthalic acid in 2 ml water was added to the reactor through the dropping funnel. The mixture was stirred for 30 min. maintaining the temperature at 60°C. 136gms of ammonium aluminium sulfate was added to the above mass along with 100ml water with vigorous stirring. The temperature of the bath was gradually raised to 70°C and heating continued for 1 hr. The pre made sulfo salicylic acid was added to the reactor and the heating was continued for 1 hour. The reaction mixture was transferred to a bucket and the pH was adjusted to 3.0 using sodium bicarbonate. The solution was filtered and dried using a spray drier at a temperature of 260°C. The dried product was packed in a plastic container.

[0058] This product was used for tanning the delimed goatskins at an offer of 1.5% as Al_2O_3 on pelt weight. The tanned leathers were aged for one day and the shrinkage temperature of the tanned leather was found to be 85°C, exhibiting 80% exhaustion of aluminium.

[0059] The following are the advantages of the present invention:

1. Cheaper and indigenously available raw materials are used for the process of the present invention ensuring its cost effectiveness.
2. Condensation step is not required and therefore complicate control measures are not required.
3. The resulting product is pure white powder, freely soluble in water ensuring its potential use as a tanning agent.
4. The process ensures the metal ion in complex form as it resists hydrolysis up to a pH in the range of 5.5-7.0.
5. Syntan moiety is a polymeric matrix, which is built up without the use of formaldehyde, ensuring that the process of the present invention results in an eco-friendly product.
6. The product of the present invention contains 10-12% Al_2O_3 and has application as a self tanning agent for delimed pelts, apart from serving as dye saver and chrome exhaust aid.
7. The product produces white and soft leathers.
8. The product can be used as self-tanning agent, co-tanning agent along with BCS to improve chromium exhaustion and as retanning agent.

9. The shelf life of the product is about 1.5-2 years
 10. Since the product has aluminium as cation with high positive charge, it can also be used as dye saver in post tanning.
 11. Since the product does not contain any active methylene groups in the organic matrix, does not undergo photo oxidation and hence the tanned leathers do not show any discoloration on aging.

Claims

1. A process for the preparation of a novel synthetic aluminium tanning agent, which comprises
 - i) sulfonating an aromatic compound having up to 14 carbon atoms followed by the addition of an aqueous mixture of organic ligands and polyfunctional polymer,
 - ii) adding trivalent aluminium salt along with water to the reaction mixture formed in step(i) and mixing the reaction mass to form a complex,
 - iii) adding sulfosalicylic acid to the reaction mixture formed in step(ii) to form a slurry,
 - iv) adjusting pH of the slurry formed in step (iii), in range of 2.5-3.0 by alkalinizing agent,
 - v) drying the slurry to obtain the tanning agent in powder form.
2. A process as claimed in claim 1 therein the sulfonation in step (i) is carried out at a temperature in the range of 25 -160°C.
3. A process as claimed in claim 1 wherein the aqueous mixture of organic ligands and polyfunctional polymer is added to the sulfonated aromatic compound at a temperature in the range of 60 - 80°C.
4. A process as claimed in claim 1 wherein the addition of trivalent aluminium salt along with water to the reaction mixture formed in step (i) is carried out at a temperature in the range of 60 - 80°C.
5. A process as claimed in claim 1 wherein the addition of sulfosalicylic acid to the reaction mixture formed in step (ii) is done at a temperature in the range of 60 - 80°C.
6. A process as claimed in claim 1 wherein the slurry obtained in step (iv) is aerated for a period of 30 - 60 min before drying at a temperature in the range of 130-260°C to get the tanning agent in powder form.
7. A process as claimed in claim 1 wherein the aromatic compound used is selected from the group consisting of phenol, phenolic acid, naphthol, naphthalene and anthracene.

8. A process as claimed in claim 1 wherein the amount of the aromatic compound used is in the range of 0.5 - 2.0 moles per mole aluminium.
9. A process as claimed in claim 1 wherein sulfonation is carried out using sulfuric acid in an amount in the range of 1- 5 moles per mole of aluminium.
10. A process as claimed in claim 1 wherein the organic ligand used is selected from the group consisting of formic acid, citric acid, phthalic acid, polycarboxylic acid, oxalic acid, salicylic acid, sodium salts thereof and any mixture thereof.
11. A process as claimed in claim 1 wherein the amount of organic ligands used is in the range of 0.001- 0.05 mole per mole of aluminium.
12. A process as claimed in claim 1 wherein the polyfunctional polymer used is selected from the group consisting of polyacrylic acid, polyacryl amide, polymethacrylic acid, and any mixture thereof
13. A process as claimed in claim 1 wherein the amount of the polyfunctional polymer used is in the range of 0.0001- 0.001 mole per mole of aluminium.
14. A process as claimed in claim 1 wherein the trivalent aluminium salt is selected from the group consisting of aluminium sulfate, aluminium chloride, aluminium ammonium sulfate and aluminium potassium sulfate.
15. A process as claimed in claim 1 wherein the amount of water added to the reaction mixture is in the range of 5 - 30 moles per mole of aluminium.
16. A process as claimed in claim 1 wherein the amount of sulfosalicylic acid used is in the range of 0.001- 0.01 moles per mole of aluminium.
17. A process as claimed in claim 1 wherein the amount of sulfuric acid used for sulfonating aromatic compound is in the range of 0.001 - 0.01 moles per mole of aluminium.
18. A process as claimed in claim 1 wherein the drying of the slurry is done by drum drying or spray drying.
19. A process as claimed in claim 1 wherein the alkalinizing agent used in step (iv) is selected from the group consisting of sodium bicarbonate, sodium sulphite and NaOH.

Patentansprüche

1. Ein Verfahren zur Herstellung eines neuartigen syn-

thetischen Aluminiumgerbmittels, welches umfasst:

- i) Sulfonieren einer aromatischen Verbindung mit bis zu 14 Kohlenstoffatomen und anschließend die Zugabe eines wässrigen Gemisches aus organischen Liganden und polyfunktionellem Polymer, 5
- ii) Zugabe von dreiwertigem Aluminiumsalz zusammen mit Wasser zu dem in Schritt (i) gebildeten Reaktionsgemisch und Mischen der Reaktionsmasse zur Bildung eines Komplexes, 10
- iii) Zugabe von Sulfosalicylsäure zu dem in Schritt (ii) gebildeten Reaktionsgemisch zur Bildung einer Aufschlammung, 15
- iv) Einstellen des pH der in Schritt (iii) gebildeten Aufschlammung auf einen Bereich von 2,5-3,0 mit einem alkalisierenden Agens, 20
- v) Trocknen der Aufschlammung zum Erhalt des Gerbmittels in Pulverform.
2. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Sulfonierung in Schritt (i) bei einer Temperatur im Bereich von 25-160°C durchgeführt wird.
3. Ein Verfahren wie in Anspruch 1 beansprucht, worin das wässrige Gemisch aus organischen Liganden und polyfunktionellem Polymer zu der sulfonierten aromatischen Verbindung bei einer Temperatur im Bereich von 60-80°C gegeben wird. 25
4. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Zugabe von dreiwertigem Aluminiumsalz zusammen mit Wasser zu dem in Schritt (i) gebildeten Reaktionsgemisch bei einer Temperatur im Bereich von 60-80°C durchgeführt wird. 30
5. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Zugabe von Sulfosalicylsäure zu dem in Schritt (ii) gebildeten Reaktionsgemisch bei einer Temperatur im Bereich von 60-80°C erfolgt. 40
6. Ein Verfahren wie in Anspruch 1 beansprucht, worin die in Schritt (iv) erhaltene Aufschlammung über einen Zeitraum von 30-60 Minuten vor dem Trocknen bei einer Temperatur im Bereich von 130-260°C belüftet wird, zum Erhalt des Gerbmittels in Pulverform. 45
7. Ein Verfahren wie in Anspruch 1 beansprucht, worin die eingesetzte aromatische Verbindung aus der Gruppe ausgewählt ist, bestehend aus Phenol, Phenolsäure, Naphthol, Naphthalen und Anthracen. 50
8. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Menge an eingesetzter aromatischer Verbindung im Bereich von 0,5-2,0 Mol pro Mol Aluminium liegt. 55
9. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Sulfonierung unter Verwendung von Schwefel-

säure in einer Menge im Bereich von 1-5 Mol pro Mol Aluminium durchgeführt wird.

10. Ein Verfahren wie in Anspruch 1 beansprucht, worin der eingesetzte organische Ligand aus der Gruppe ausgewählt ist, bestehend aus Ameisensäure, Citronensäure, Phthalsäure, Polycarbonsäure, Oxalsäure, Salicylsäure, Natriumsalzen davon und einem beliebigen Gemisch davon.
11. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Menge eingesetzter organischer Liganden im Bereich von 0,001-0,05 Mol pro Mol Aluminium liegt.
12. Ein Verfahren wie in Anspruch 1 beansprucht, worin das eingesetzte polyfunktionelle Polymer aus der Gruppe ausgewählt ist, bestehend aus Polyacrylsäure, Polyacrylamid, Polymethacrylsäure und einem beliebigen Gemisch davon.
13. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Menge an eingesetztem polyfunktionellen Polymer im Bereich von 0,0001-0,001 Mol pro Mol Aluminium liegt.
14. Ein Verfahren wie in Anspruch 1 beansprucht, worin das dreiwertige Aluminiumsalz aus der Gruppe ausgewählt ist, bestehend aus Aluminiumsulfat, Aluminiumchlorid, Aluminiumammoniumsulfat und Aluminiumkaliumsulfat.
15. Ein Verfahren wie in Anspruch 1 beansprucht, worin die zu dem Reaktionsgemisch gegebene Wassermenge im Bereich von 5-30 Mol pro Mol Aluminium liegt.
16. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Menge an eingesetzter Sulfosalicylsäure im Bereich von 0,001-0,01 Mol pro Mol Aluminium liegt.
17. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Menge der zur Sulfonierung der aromatischen Verbindung eingesetzten Schwefelsäure im Bereich von 0,001-0,01 Mol pro Mol Aluminium liegt.
18. Ein Verfahren wie in Anspruch 1 beansprucht, worin die Trocknung der Aufschlammung mittels Trommeltrocknung oder Sprühtrocknung erfolgt.
19. Ein Verfahren wie in Anspruch 1 beansprucht, worin das in Schritt (iv) eingesetzte alkalisierende Agens aus der Gruppe ausgewählt ist, bestehend aus Natriumbicarbonat, Natriumsulfit und NaOH.

Revendications

1. Procédé de préparation d'un nouvel agent de tan-

nage en aluminium de synthèse, qui comprend

- i) sulfoner un composé aromatique ayant jusqu'à 14 atomes de carbone, puis ajout d'un mélange aqueux de ligands organiques et de polymère polyfonctionnel, 5
 - ii) ajouter du sel d'aluminium trivalent en même temps que de l'eau au mélange réactionnel formé à l'étape (i) et mélanger la masse réactionnelle pour former un complexe, 10
 - iii) ajouter de l'acide sulfosalicylique au mélange réactionnel formé à l'étape (ii) pour former une bouillie, 15
 - iv) ajuster le pH de la bouillie formée à l'étape (iii), dans une plage de 2,5-3,0 par un agent d'alcalinisation,
 - v) sécher la bouillie pour obtenir l'agent de tannage sous forme de poudre.
2. Procédé selon la revendication 1, dans lequel la sulfonation de l'étape (i) est effectuée à une température dans la plage de 25 - 160°C. 20
 3. Procédé selon la revendication 1, dans lequel le mélange aqueux de ligands organiques et de polymère polyfonctionnel est ajouté au composé aromatique sulfoné à une température dans la plage de 60 - 80°C. 25
 4. Procédé selon la revendication 1, dans lequel l'ajout de sel d'aluminium trivalent et d'eau au mélange réactionnel formé à l'étape (i) est effectué à une température dans la plage de 60 - 80°C. 30
 5. Procédé selon la revendication 1, dans lequel l'ajout d'acide sulfosalicylique au mélange réactionnel formé à l'étape (ii) est effectué à une température dans la plage de 60 - 80°C. 35
 6. Procédé selon la revendication 1, dans lequel la bouillie obtenue à l'étape (iv) est aérée pendant une période de 30 - 60 minutes avant séchage à une température dans la plage de 130-260°C pour obtenir l'agent de tannage sous forme de poudre. 40
 7. Procédé selon la revendication 1, dans lequel le composé aromatique utilisé est choisi dans le groupe constitué par le phénol, l'acide phénolique, le naphthol, le naphthalène et l'anthracène. 45
 8. Procédé selon la revendication 1, dans lequel la quantité du composé aromatique utilisé est dans la plage de 0,5 - 2,0 moles par mole d'aluminium. 50
 9. Procédé selon la revendication 1, dans lequel la sulfonation est effectuée en utilisant de l'acide sulfurique dans une quantité dans la plage de 1 - 5 moles par mole d'aluminium. 55
 10. Procédé selon la revendication 1, dans lequel le ligand organique utilisé est choisi dans le groupe constitué par l'acide formique, l'acide citrique, l'acide phtalique, l'acide polycarboxylique, l'acide oxalique, l'acide salicylique, les sels de sodium de ceux-ci et tout mélange de ceux-ci.
 11. Procédé selon la revendication 1, dans lequel la quantité de ligands organiques utilisée se trouve dans la plage de 0,001 - 0,05 mole par mole d'aluminium.
 12. Procédé selon la revendication 1, dans lequel le polymère polyfonctionnel utilisé est choisi dans le groupe constitué par l'acide polyacrylique, le polyacrylamide, l'acide polyméthacrylique et tout mélange de ceux-ci.
 13. Procédé selon la revendication 1, dans lequel la quantité du polymère polyfonctionnel utilisée se trouve dans la plage de 0, 0001 - 0,001 mole par mole d'aluminium.
 14. Procédé selon la revendication 1, dans lequel le sel d'aluminium trivalent est choisi dans le groupe constitué par le sulfate d'aluminium, le chlorure d'aluminium, le sulfate d'ammonium d'aluminium et le sulfate de potassium d'aluminium.
 15. Procédé selon la revendication 1, dans lequel la quantité d'eau ajoutée au mélange de réaction se trouve dans la plage de 5 - 30 moles par mole d'aluminium.
 16. Procédé selon la revendication 1, dans lequel la quantité d'acide sulfosalicylique utilisée se trouve dans la plage de 0,001 - 0,01 mole par mole d'aluminium.
 17. Procédé selon la revendication 1, dans lequel la quantité d'acide sulfurique utilisée pour sulfoner le composé aromatique se trouve dans la plage de 0,001 - 0,01 mole par mole d'aluminium.
 18. Procédé selon la revendication 1, dans lequel le séchage de la bouillie est effectué par séchage au tambour ou séchage par pulvérisation.
 19. Procédé selon la revendication 1, dans lequel l'agent d'alcalinisation utilisé à l'étape (iv) est choisi dans le groupe constitué par le bicarbonate de sodium, le sulfure de sodium et le NaOH.

REFERENCES CITED IN THE DESCRIPTION

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