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(54) METHOD FOR PRODUCING REPTILE LEATHER OR LEATHER PRODUCT USING HEXAVALENT CHROMIUM TREATMENT AGENT, AND REPTILE LEATHER OR LEATHER PRODUCT USING HEXAVALENT CHROMIUM TREATMENT AGENT

(57) Provided is a method for producing a reptile leather, in which a leather can be treated with a hexavalent chromium treatment agent in the course of leather production without change in the visual appearance of the leather. The method for producing a reptile leather according to the present invention comprises: a chrome tanning step of performing chrome tanning on reptile skin to obtain a leather; a dyeing-fatliquoring step of performing dyeing and fatliquoring simultaneously on the leather subjected to the chrome tanning; and a finishing step of performing finishing on the leather subjected to the dyeing and fatliquoring, the method further comprising a hexavalent chromium treatment step of, prior to the finishing step, applying a hexavalent chromium-reducing compound capable of reducing hexavalent chromium into trivalent chromium to the leather subjected to the chrome tanning in the chrome tanning step.

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Description

Technical Field

[0001] The present invention relates to a method for producing a reptile leather or leather article using a hexavalent chromium treatment agent and to a reptile leather or leather article produced using a hexavalent chromium treatment agent.

Background Art

[0002] Leather articles are used in various products such as watchbands and handbags. In particular, the visual appearance of the leather enhances the commercial value of watchbands and handbags, increasing the level of satisfaction of consumers. It is needless to say that such products are designed to allow the leather to be in direct touch with the user's skin and that the feel of the leather against the skin further enhances an added value to the products.

[0003] Production of such a leather article entails making a large leather sheet in advance. In the leather production, an animal skin to be used in the leather article, such as the skin of crocodile or cow, is obtained first. The skin as obtained has low durability and cannot be used by itself. Thus, the skin is subjected to tanning. This tanning imparts heat resistance and durability to the skin, so that a leather is produced from the skin. The leather thus obtained is dyed with a desired color, or the surface texture of the leather is modified. In this manner, a sheet of leather is obtained. When this sheet is used to produce a leather article, for example, a process is performed in which the sheet is cut into a shape suitable for the intended use, and the cut sheet is attached to a core material or the like with an adhesive. Such a technique for production of leather articles has been traditionally used and is widely known.

[0004] Tanning is a technique for obtaining a durable leather by treating skin. Tannin acquired from plants had been used in the past; however, treatment with tannin fails to achieve sufficient heat resistance, flexibility, and elasticity. Recently, therefore, chrome tanning that uses a chromium tanning agent (basic chromium sulfate) and that can achieve high heat resistance, flexibility, and elasticity has become mainstream. The chrome tanning is employed for more than 90% of tanning treatments performed throughout the world and has the greatest economical importance. A hydrated chromium complex is embedded between carboxyl groups of glutamic acid and aspartic acid in a collagen peptide structure, so that a soft, durable leather is obtained. The method for chrome tanning is widely well-known and is described, for example, in Non Patent Literature 1.

[0005] High-quality leathers or leather articles with excellent heat resistance, flexibility, and elasticity are obtained typically through chrome tanning. Chrome tanning agents for chrome tanning contain chromium; thus, a large amount of chromium remains in a leather or leather article subjected to tanning using a chrome tanning agent.

[0006] Chromium is trivalent in chrome tanning agents. The trivalent chromium may be oxidized into hexavalent chromium through heating or bonding in the process of production of leathers or leather articles. Additionally, hexavalent chromium present as an impurity in chrome tanning agents may be incorporated in leathers or leather articles. Other than such hexavalent chromium incorporated through the process of production of leathers or leather articles, there is hexavalent chromium produced by the fact that trivalent chromium in the leathers or leather articles is oxidized, for example, by light, heat, or high temperature and humidity. The presence of hexavalent chromium can be examined by a measurement test. Trivalent chromium is non-toxic, while hexavalent chromium is toxic. When contacting the skin or mucous membranes, hexavalent chromium can induce skin roughness or allergy and, in severe cases, cause dermatitis or tumor. Thus, hexavalent chromium significantly affects the human body. Even a small amount of hexavalent chromium is considered to have all hazard risks including carcinogenicity, mutagenicity, and reproductive toxicity. Due to its toxicity, hexavalent chromium is specified as a banned substance.

[0007] Under the above circumstances, EU regulations on hexavalent chromium in leathers or leather articles were published as Regulations (EU), No. 3014/2014 in the Official Journal of European Union on March 26, 2014. Concerning leather articles and products containing a leather in a part to be in contact with the skin, the Regulations specify that leather articles containing 3 mg/kg (3 ppm) or more of chromium(VI) oxide with respect to the total dry weight of the leather and leather part shall be restricted as of May 1, 2015 from the viewpoint of impacts on the human body (in particular, irritation to skin). The Regulations state that the method according to EN ISO 17075 is the only international standard analysis method currently available for quantification of hexavalent chromium in leathers or leather articles ((6) in the Regulations).

[0008] Under these circumstances, Patent Literature 1 states in Example 2 that placement of a drop of an aqueous solution of ascorbic acid on a tanned leather detoxified hexavalent chromium contained in the leather.

Citation List

Patent Literature

[0009] Patent Literature 1: Japanese Patent Laid-Open No. 2008-231388

Non Patent Literature

[0010] Non Patent Literature 1: "Knowledge of Leather", the Japanese Association of Leather Technology (retrieved online on December 14, 2015), Internet URL: <http://www.hikaku-kyo.org/htdoc/hikakunochisiki-04.htm>

Summary of Invention

Technical Problem

[0011] When a leather, in particular a reptile leather, is treated with a hexavalent chromium treatment agent containing a hexavalent chromium-reducing compound such as ascorbic acid, the treatment may cause a change in the visual appearance of the leather.

[0012] It is therefore an object of the present invention to provide a method for producing a reptile leather, in which a leather can be treated with a hexavalent chromium treatment agent in the course of leather production without change in the visual appearance of the leather.

Solution to Problem

[0013] A method for producing a reptile leather according to the present invention comprises: a chrome tanning step of performing chrome tanning on reptile skin to obtain a leather; a dyeing-fatliquoring step of performing dyeing and fatliquoring simultaneously on the leather subjected to the chrome tanning; and a finishing step of performing finishing on the leather subjected to the dyeing and fatliquoring, the method further comprising a hexavalent chromium treatment step of, prior to the finishing step, applying a hexavalent chromium-reducing compound capable of reducing hexavalent chromium into trivalent chromium to the leather subjected to the chrome tanning in the chrome tanning step.

Advantageous Effects of Invention

[0014] With the method for producing a reptile leather according to the present invention, a leather can be treated with a hexavalent chromium treatment agent in the course of leather production without change in the visual appearance of the leather.

Description of Embodiments

<Method for Producing Leather>

<Preferred Embodiment [1]>

[0015] First, a preferred embodiment of the present invention will be described.

[0016] A method according to a preferred embodiment of the present invention comprises a chrome tanning step, dyeing-fatliquoring step, and finishing step. The method according to the present embodiment further comprises a hexavalent chromium treatment step of applying a hexavalent chromium-reducing compound capable of reducing hexavalent chromium into trivalent chromium to the leather subjected to the chrome tanning in the chrome tanning step, and the dyeing-fatliquoring step and hexavalent chromium treatment step are simultaneously performed.

[0017] The chrome tanning step is a step of performing chrome tanning on reptile skin to obtain a leather. Examples of the skin used in this step include the skin of reptiles such as sea turtles belonging to the family Cheloniidae of the order Testudines, monitor lizards belonging to the family Varanidae of the suborder Lacertilia, tegus belonging to the family Teiidae of the suborder Lacertilia, Python reticulatus and Python molurus belonging to the family Boidae of the suborder Serpentes, sea snakes such as Laticauda semifasciata belonging to the family Hydrophiidae of the suborder Serpentes, water snakes belonging to the family Homalopsidae of the suborder Serpentes, Freshwater crocodile belonging to the family Crocodylidae of the order Crocodilia, and American alligator and caiman belonging to the family Alligatoridae of the order Crocodilia. The chrome tanning can be accomplished by an ordinary method.

[0018] In the dyeing-fatliquoring step, dyeing and fatliquoring are simultaneously performed on the leather subjected to the chrome tanning. Through this step, the leather is dyed with a color material and endowed with properties such as flexibility. Performing dyeing and fatliquoring simultaneously offers the advantage of reducing the number of processes. The method according to the present embodiment further comprises a hexavalent chromium treatment step of applying a hexavalent chromium-reducing compound to the leather. Through this step, hexavalent chromium which can be contained in the leather after the chrome tanning is converted to trivalent chromium. The fact that performing the hexavalent chromium treatment step simultaneously with the dyeing-fatliquoring step offers the advantage of further reducing the number of processes.

[0019] In the finishing step, finishing is performed on the leather subjected to the dyeing and fatliquoring. For example, the matte color resulting from the dyeing-fatliquoring step is changed to a glossy color, or so-called "scale", a three-dimensional appearance characteristic of reptile skin, is imparted to the leather.

[0020] Specific examples of the process performed include the process of polishing the grain side of the leather with agate or glass to impart gloss to the leather (glazing finish), the process of pressing a heated metal roller on the leather to impart gloss to the leather, or the process of rubbing the leather with a heated felt roller to impart gloss to the leather. Next, if necessary, the side of the leather opposite to the grain side is shaved, and then the leather is placed on a hot plate typically set at 100°C or higher, preferably set at 120 to 130°C. This can impart the three-dimensional appearance called "scale" to the leather.

[0021] As described above, the finishing step generally involves heating the leather. Thus, trivalent chromium contained in the leather after the chrome tanning may be changed into hexavalent chromium. Even in this case, however, the hexavalent chromium thus produced can be reconverted to trivalent chromium by the action of the hexavalent chromium-reducing compound incorporated in the leather through the hexavalent chromium treatment step.

[0022] In the present embodiment, the hexavalent chromium treatment step precedes the finishing step, and thus the leather’s visual appearance obtained by the finishing step can be maintained without being impaired. Among reptile leathers which can be used in the present invention, leathers of animals (crocodiles) belonging to the order Crocodilia of the class Reptilia are expensive and have a delicate appearance, and are preferably not subjected to any other process after the finishing. Thus, the method according to the present embodiment in which the hexavalent chromium treatment step precedes the finishing step is particularly suitable for use in production of crocodile leathers.

[0023] Hereinafter, the dyeing-fatliquoring step and hexavalent chromium treatment step which are simultaneously performed in the present embodiment will be described in more detail.

[Dyeing-Fatliquoring Step and Hexavalent Chromium Treatment Step]

[0024] In the dyeing-fatliquoring step and hexavalent chromium treatment step, it is typical to use a hexavalent chromium treatment agent for simultaneously accomplishing the two steps. The hexavalent chromium treatment agent used for simultaneously accomplishing the two steps is specifically referred to herein as a "simultaneous treatment agent".

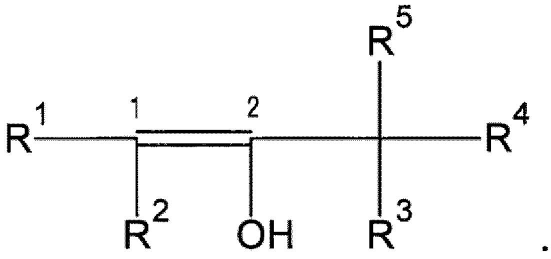
[0025] The simultaneous treatment agent contains water, a color material commonly used in dyeing of leathers, and an oil commonly used in fatliquoring of leathers. Furthermore, a surfactant commonly used for simultaneously accomplishing dyeing and fatliquoring and a hexavalent chromium-reducing compound for accomplishing hexavalent chromium treatment are added to the simultaneous treatment agent.

[0026] The hexavalent chromium-reducing compound is a compound capable of reducing hexavalent chromium into trivalent chromium.

[0027] Examples of such a hexavalent chromium-reducing compound include compounds proposed by the present inventors (International Application No. PCT/JP2015/71509, international filing date: July 29, 2015) in addition to ascorbic acid described in Patent Literature 1. Hereinafter, the hexavalent chromium-reducing compound proposed by the present inventors will be described.

[0028] The hexavalent chromium-reducing compound is a compound capable of reducing hexavalent chromium into trivalent chromium, and examples of the compound include an organic compound (A) represented by formula (1) below. This compound is composed of at least C, O, H atoms capable of acting to reduce hexavalent chromium into trivalent chromium (having the ability to reduce hexavalent chromium into trivalent chromium), has a single bond and double bond among three carbon atoms, and has a hydroxy group linked to the central carbon atom. The structure represented by formula (1) acts to reduce hexavalent chromium into trivalent chromium.

[Formula 1]



. . . (1)

[0029] In formula (1), R^1, R^2, R^3, R^4, and R^5 are each independently a substituent composed of C, H, O (substituent composed of C, H, and optionally O), preferably contain a carbonyl group having an unsaturated bond, and have no reactive functional groups such as an aldehyde group and a carboxyl group. It is also preferable that R^1, R^2, R^3, R^4, and R^5 have no functional groups including nitrogen-containing groups such as an amine group and an isocyanate group and sulfur-containing groups such as a sulfate group. R^1 or R^2 and R^3, R^4, or R^5 may be linked together to form a ring.

[0030] The compound having the structure represented by formula (1) may be a cyclic hydrocarbon or may be also an aromatic hydrocarbon having a monocyclic ring or fused ring. When the compound is an aromatic hydrocarbon, the π bond is, in effect, delocalized without staying in the double bond between the carbon atoms 1 and 2 in formula (1). The cyclic hydrocarbon or aromatic hydrocarbon may have a substituent.

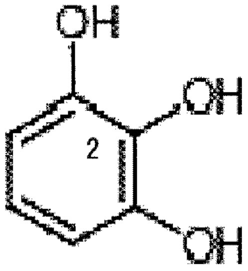
[0031] It is preferable that the organic compound (A) have the structure represented by formula (1) and a hydroxy group and have no reactive functional groups such as an aldehyde group and a carboxyl group in the structure.

[0032] It is preferable that the hexavalent chromium-reducing compound comprise, in addition to the organic compound (A), an organic compound (B) that has the structure represented by formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium and that has no hydroxyphenyl groups, no aldehyde groups, and no carboxyl groups. The organic compound (B) preferably has no functional groups including nitrogen-containing groups such as an amine group and an isocyanate group and sulfur-containing groups such as a sulfate group.

[0033] Examples of the organic compound (A) or (B) include the following compounds (formulas (2) to (14)) and derivatives thereof. In the present invention, it is also preferable to use a mixture of two or more of these compounds and derivatives thereof.

[Formula 2]

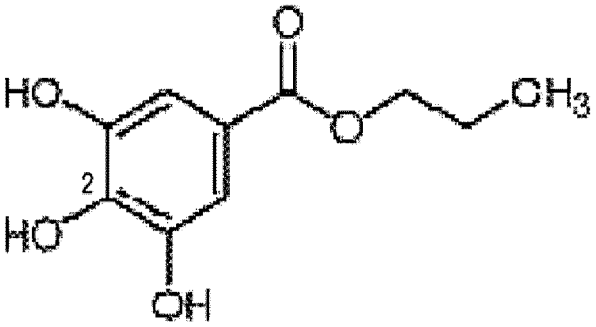
- Pyrogallol



. . . (2)

[Formula 3]

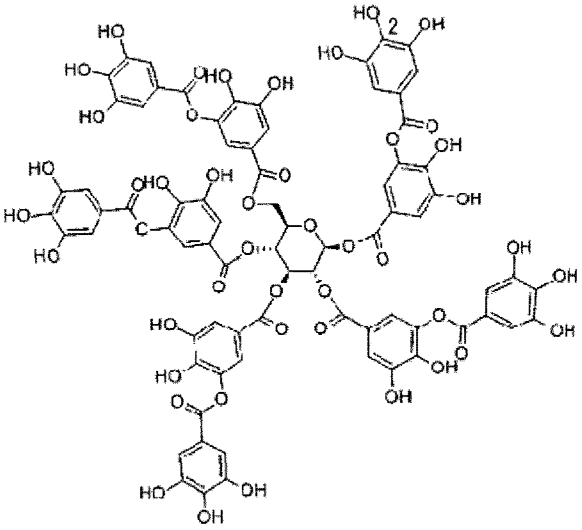
・Propyl gallate



・・・(3)

[Formula 4]

・Tannic acid



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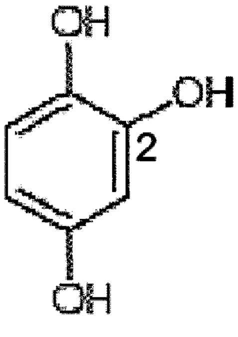
[Formula 5]

・1,2,4-Trihydroxybenzene



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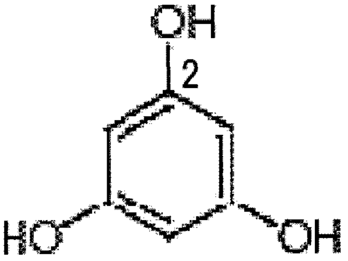
[Formula 6]

・Phloroglucinol



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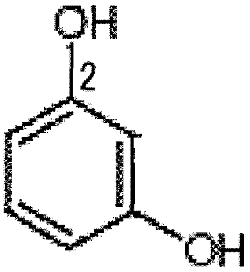
[Formula 7]

・Resorcinol



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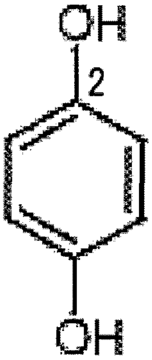
[Formula 8]

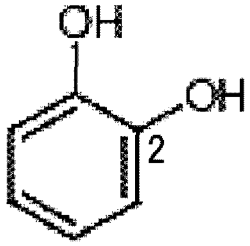
・Hydroquinone



・・・(8)

[Formula 9]

・Catechol



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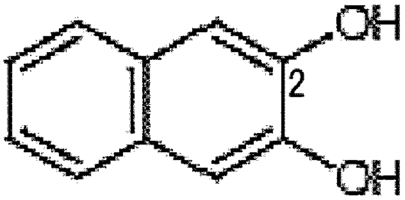
[Formula 10]

. 2,3-Dihydroxynaphthalene



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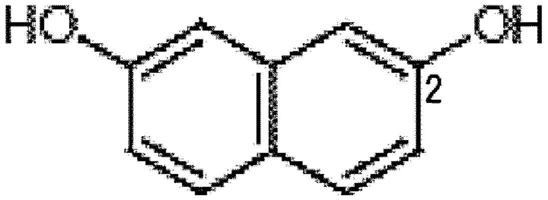
[Formula 11]

. 2,7-Dihydroxynaphthalene



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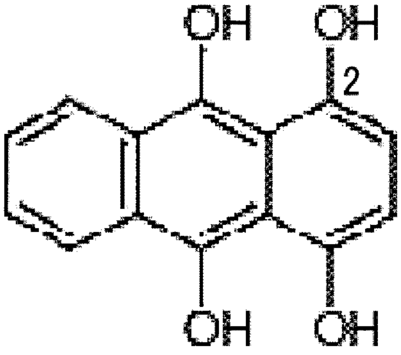
[Formula 12]

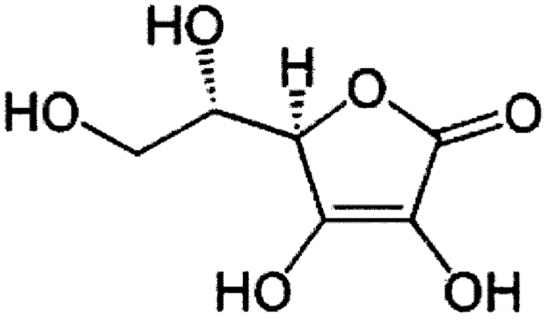
• 1,4,9,10-Anthracenetetrol



...(12)

[Formula 13]

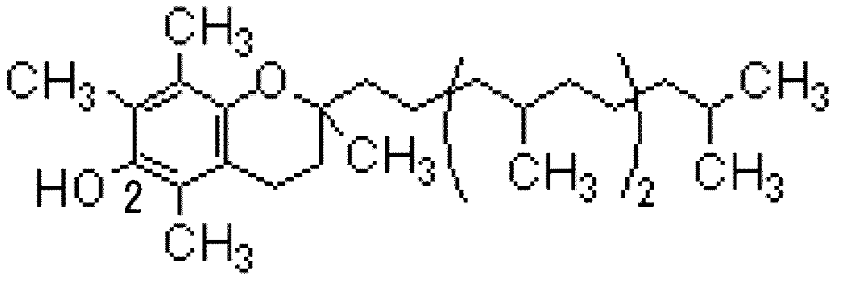
• Ascorbic acid



...(13)

[Formula 14]

• Tocopherol



...(14)

[0034] The carbon atom 2 in formulas (2) to (12) and (14) corresponds, for example, to the carbon atom 2 in formula (1).

[0035] The hexavalent chromium-reducing compound is an organic compound acting on hexavalent chromium, which is toxic, to chemically convert it into a non-toxic compound. For example, this hexavalent chromium-reducing compound can detoxify hexavalent chromium by reducing it into trivalent chromium.

[0036] Generally known reducing agents include lithium aluminum hydride, sodium borohydride, hydrazine, dibutylaluminum hydride, oxalic acid, and formic acid. The use of these typical reducing agents poses various problems.

[0037] When lithium aluminum hydride is used as a reducing agent, the agent is a strong reducing agent in the form of a powder. This reducing agent is dangerous because it reacts vigorously with water to produce hydrogen which is flammable. Such an agent that produces a flammable substance in this manner is unsuitable for use in leathers or leather articles which, in general, are often brought into contact with the skin (sweat) or exposed to rain.

[0038] When sodium borohydride is used as a reducing agent, the agent is somewhat hygroscopic and prone to degradation by water. The agent must therefore be stored in a sealed condition. An aqueous solution produced by contact of the agent with a water-containing substance such as sweat or rain is strongly basic, because the solution contains a degradation product of the agent. The agent can thus cause adverse effects on dermis (skin) and mucous membranes. When placed under acidic or neutral conditions, the agent is degraded to produce hydrogen; thus, the agent must be stored in an alkaline solution and cannot be contained in leathers or leather articles. The agent is also difficult to handle, because it is degraded by water to produce hydrogen.

[0039] Hydrazine is a colorless liquid with a pungent odor similar to that of ammonia, and releases white smoke when contacted with air. Hydrazine is therefore unsuitable for use. Additionally, hydrazine is difficult to handle because it is easily soluble in water, has high reducing capacity, is easily degradable, and is flammable.

[0040] When dibutylaluminum hydride is used as a reducing agent, the agent is a colorless liquid but is susceptible to humidity. The agent should therefore be stored and used in an inert gas atmosphere and is difficult to use in an ordinary air atmosphere.

[0041] When oxalic acid is used as a reducing agent, the agent is poisonous because it strongly binds to calcium ions in blood in the human body. Oxalic acid is designated as a non-medical deleterious substance under Poisonous and Deleterious Substances Control Law. The use of such a poisonous substance in leathers or leather articles is unsuitable for the intended purpose.

[0042] When formic acid is used as a reducing agent, the formic acid solution or formic acid vapor is harmful to the skin and eyes and can, in particular, do irreparable damage to the eyes. Additionally, inhalation of formic acid can cause a disorder such as pulmonary edema. Formic acid is therefore unsuitable for use. Moreover, chronic exposure to formic acid is considered to adversely affect the liver and kidney, and formic acid is also considered as a possible allergen. Formic acid is therefore unsuitable for the purpose of the present invention.

[0043] With these facts in mind, the present applicant conducted various investigations and experiments on hexavalent chromium-reducing compounds usable in leathers or leather articles and has found compounds suited for the intended purpose.

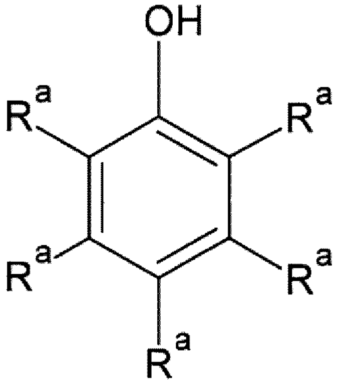
[0044] The organic compounds (A) and (B) comprised as the hexavalent chromium-reducing compound not only have the primary ability to treat and detoxify hexavalent chromium, but also are free of toxicity and cause no disorder such as skin roughness when leathers or leather articles treated with these compounds is in contact with the skin. The compounds (A) and (B) are preferably compounds that do not degrade each other by their reducing capacity and that are not reactive or interactive with each other. Such an organic compound is preferably a compound having a basic skeleton represented by formula (1) above and more preferably a stable compound comprising C, H, O atoms.

[0045] The organic compound having the structure represented by formula (1) has no functional groups such as an aldehyde group and a carboxyl group. It is preferable that the organic compound have no functional groups including nitrogen-containing groups such as an amine group and an isocyanate group and sulfur-containing groups such as a sulfate group. These functional groups are reactive and can undergo an unexpected reaction during use of leathers or leather articles, thus being unsuitable for hexavalent chromium-reducing compounds. The organic compound is capable of acting on hexavalent chromium to produce a compound not detected as a hexavalent chromium compound, thereby detoxifying hexavalent chromium.

(Organic Compound (A))

[0046] The organic compound (A) has the structure represented by formula (1) above and further has, for example, a hydroxyphenyl group represented by formula (15) below. With this functional group, the organic compound (A), when incorporated in leathers or leather articles, takes effect immediately, remains stable for a long time, maintains its reducing effect over a long period of time, and provides high heat resistance. Formation of hexavalent chromium is thus inhibited over a long period of time. Additionally, the organic compound (A) contained in leathers or leather articles is resistant to degradation by water-containing substances such as sweat and rain. The reason for these beneficial effects has not been clarified; however, the following hypothesis is formulated based on the fact that collagen, which is a main component of leathers, is, in general, chemically cross-linked and stabilized as a result of tanning: The organic compound (A) can remain for a long time, particularly thanks to the high interactivity of its hydroxyphenyl group with the collagen, while the organic compound (A) is incorporated in the collagen not completely but in such a manner that the organic compound (A) forms an island of a sea-island structure and is allowed a degree of freedom sufficient to exhibit the reducing capacity. Since the organic compound (A) is used in leathers or leather articles, a safe compound having low environmental impact is preferred as the organic compound (A).

[Formula 15]



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[0047] In formula (15), R^a is a monovalent group or a divalent group. Examples of the monovalent group include a hydrogen atom, a hydrocarbon group, and an oxygen-containing group. Examples of the divalent group include a divalent hydrocarbon group and a divalent oxygen-containing group. Among these examples, a hydrogen atom, a monovalent hydrocarbon group, a divalent hydrocarbon group, or a hydroxy group is preferred to achieve higher compatibility with leathers or leather articles. A plurality of R^a are independent from each other and may be the same or different. Adjacent R^a groups may be linked together to form an aromatic ring or aliphatic ring. R^a may be linked to R^a of another hydroxyphenyl group. It is preferable that not all the R^a groups be a hydrogen atom. In order that the organic compound (A) may take effect more immediately and exhibit higher reducing capacity stably over a long period of time in leathers or leather articles, the group represented by formula (15) is more preferably a dihydroxyphenyl group or trihydroxyphenyl group and even more preferably a 3,4,5-trihydroxyphenyl group.

[0048] Preferred as the hydrocarbon group is a C_1 to C_{20} hydrocarbon group, and specific examples thereof include a C_1 to C_{20} alkyl group, a C_7 to C_{20} arylalkyl group, or an unsubstituted or substituted C_6 to C_{20} aryl group. Examples of the hydrocarbon group include a methyl group, an ethyl group, a n-propyl group, an isopropyl group, an allyl group, a n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an amyl group, a n-pentyl group, a neopentyl group, a n-hexyl group, a n-heptyl group, a n-octyl group, a n-nonyl group, a n-decanyl group, a 3-methylpentyl group, a 1,1-diethylpropyl group, a 1,1-dimethylbutyl group, a 1-methyl-1-propylbutyl group, a 1,1-dipropylbutyl group, a 1,1-dimethyl-2-methylpropyl group, a 1-methyl-1-isopropyl-2-methylpropyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a norbornyl group, an adamantyl group, a phenyl group, an o-tolyl group, a m-tolyl group, a p-tolyl group, a xylyl group, an isopropylphenyl group, a t-butylphenyl group, a naphthyl group, a biphenyl group, a tert-phenyl group, a phenanthryl group, an anthracenyl group, a benzyl group, and a cumyl group. Examples of the hydrocarbon group further include hydrocarbon groups (an alkoxy group, for example) containing an oxygen-containing group such as a methoxy group, an ethoxy group, or a phenoxy group. Other examples of the hydrocarbon group include hydrocarbon groups containing an unsaturated carboxylic acid ester such as methyl ester, ethyl ester, n-propyl ester, isopropyl ester, n-butyl ester, isobutyl ester, or (5-norbornen-2-yl) ester (when the unsaturated carboxylic acid is a dicarboxylic acid, the ester may be either a monoester or diester).

[0049] An example of the oxygen-containing group is a hydroxy group.

[0050] Examples of the organic compound (A) include:

the compounds of formulas (2) to (12) and (14);

phenol, o-cresol, m-cresol, p-cresol, 2,3-dimethylphenol, 2,5-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2,4-dimethylphenol, 2,6-dimethylphenol, 2,3,5-trimethylphenol, 3,4,5-trimethylphenol, 2-tert-butylphenol, 3-tert-butylphenol, 4-tert-butylphenol, BHT (dibutylhydroxytoluene), BHA (butylhydroxyanisole), 2-phenylphenol, 3-phenylphenol, 4-phenylphenol, 3,5-diphenylphenol, 2-naphthylphenol, 3-naphthylphenol, 4-naphthylphenol, 4-tritylphenol, 2-methylresorcinol, 4-methylresorcinol, 5-methylresorcinol, 4-tert-butylcatechol, 2-methoxyphenol, 3-methoxyphenol, 2-propylphenol, 3-propylphenol, 4-propylphenol, 2-isopropylphenol, 3-isopropylphenol, 4-isopropylphenol, 2-methoxy-5-methylphenol, 2-tert-butyl-5-methylphenol, thymol, isothymol, 1-naphthol, 2-naphthol, 2-methyl-1-naphthol, 4-methoxy-1-naphthol, and 7-methoxy-2-naphthol;

dihydroxynaphthalenes such as 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, and 2,6-dihydroxynaphthalene;

tetrahydroxynaphthalenes such as 1,3,6,8-tetrahydroxynaphthalene;

methyl 3-hydroxy-naphthalene-2-carboxylate, 9-hydroxyanthracene, 1-hydroxypyrene, 1-hydroxyphenanthrene, 9-hydroxyphenanthrene, bisphenolfluorene, and phenolphthalein;
benzophenone derivatives such as 2,3,4-trihydroxybenzophenone and 2,2',3,4-tetrahydroxybenzophenone;
tannins such as catechol tannin, pyrogallol tannin, oak gall tannin, gallic tannin, and phlorotannin;
flavonoids such as anthocyanin, rutin, quercetin, fisetin, daidzein, hesperetin, hesperidin, chrysin, and flavonol;
catechins such as catechin, gallocatechin, catechin gallate, epicatechin, epigallocatechin, epicatechin gallate, epigallocatechin gallate, procyanidin, and theaflavin;
curcumin and lignan;
rhododendrol [4-(p-hydroxyphenyl)-2-butanol];
acylated rhododendrols such as acetyl rhododendrol, hexanoyl rhododendrol, octanoyl rhododendrol, dodecanoyl rhododendrol, tetradecanoyl rhododendrol, hexadecanoyl rhododendrol, octadecanoyl rhododendrol, 4-(3-acetoxybutyl)phenyl acetate, 4-(3-propanoyloxybutyl)phenyl propanoate, 4-(3-octanoyloxybutyl)phenyl octanoate, and 4-(3-palmitoyloxybutyl)phenyl palmitate;
alkyl ethers of rhododendrol such as 4-(3-methoxybutyl)phenol, 4-(3-ethoxybutyl)phenol, and 4-(3-octyloxybutyl)phenol;
rhododendrol glycosides such as rhododendrol-D-glucoside (α- or β-glycoside), rhododendrol-D-galactoside (α- or β-glycoside), rhododendrol-D-xyloside (α- or β-glycoside), and rhododendrol-D-maltoside (α- or β-glycoside); and
α-tocopherol, β-tocopherol, γ-tocopherol, and δ-tocopherol.

[0051] Other examples of the organic compound (A) include derivatives of the above substances, such as compounds having an alkoxy group and esterified products. Specific examples of the derivatives include pyrogallol-1,3-dimethyl ether, pyrogallol-1,3-diethyl ether, and 5-propylpyrogallol-1-methyl ether.

[0052] Examples of the organic compound (A) include compounds with the structure represented by formula (2) above (1,2,3-trihydroxybenzene skeleton) and derivatives thereof. Such compounds have the ability to remove hexavalent chromium.

[0053] Examples of the derivatives include those having a substituent such as a hydrocarbon group or oxygen-containing group at the 4-, 5-, 6-positions of the compound represented by formula (2) above. Preferred examples of the substituent include a C_1 to C_{20} hydrocarbon group, a C_1 to C_{20} alkoxy group, and a C_1 to C_{20} esterified product, and more preferred examples include a C_1 to C_{10} hydrocarbon group, a C_1 to C_{20} alkoxy group, and a C_1 to C_{10} esterified product. These groups are as described above. The same applies to derivatives of compounds described later. Examples of the derivatives include: a gallic acid ester such as the compound represented by formula (3) above; and the compound represented by formula (4) above which has a plurality of the structures represented by formula (2) above per molecule and derivatives of the compound of formula (4). Specific examples include catechol tannin, pyrogallol tannin, oak gall tannin, gallic tannin, and phlorotannin.

[0054] As indicated above, the substituents introduced at the 4-, 5-, 6-positions can be those suitable for the way in which the organic compound (A) is used. For example, when the compound is used by being dissolved in an ester solvent, an ester group can be introduced to increase the compatibility with the solvent.

[0055] In the present invention, the organic compound (A) preferably comprises (i) a gallic acid ester and (ii) at least one compound selected from tannic acid and a derivative thereof, and more preferably comprises (i) a gallic acid ester and (ii) tannic acid.

[0056] The gallic acid ester has a relatively low molecular weight and may therefore be considered likely to bleed out of leathers or leather articles. However, the gallic acid ester can, due to having a structural moiety corresponding to tannic acid, favorably interact with the tannic acid or derivative thereof and become unlikely to bleed out while maintaining the reducing power. When incorporated in leathers or leather articles, the gallic acid ester has reducing power and takes effect immediately. The reducing power of the gallic acid ester is not as high as that of ascorbic acid, but higher than that of tannic acid; thus, the gallic acid ester can continue to exhibit reducing power over a long period of time even after degradation and loss of reducing power of ascorbic acid (the gallic acid ester can again reduce hexavalent chromium ions newly produced by oxidation). When incorporated in leathers or leather articles, the gallic acid ester is resistant to water-containing substances such as sweat and rain and unlikely to be degraded.

[0057] The tannic acid and derivative thereof are bulky, and as seen from the fact that they are conventionally used in tanning, they have high affinity to collagen in leathers or leather articles and are unlikely to bleed out. When incorporated in leathers or leather articles, the tannin acid and derivative thereof can maintain their reducing power over a long period of time. They can therefore inhibit formation of hexavalent chromium over a longer period of time. The tannic acid and derivative thereof have low potential to irritate humans (the skin) and are safe. As for the reducing power, the tannic acid and derivative thereof takes effect slowly as compared to ascorbic acid and the gallic acid ester. However, the tannic acid and derivative thereof have high affinity to leather and leather articles and are resistant to degradation; therefore, the tannic acid and derivative thereof have a higher potential to maintain the reducing power until leather articles fulfil their function and purpose, than ascorbic acid and the gallic acid ester.

[0058] When comprising these compounds, therefore, the organic compound (A) has a high ability to penetrate into leathers or leather articles and is capable of remaining in leathers or leather articles for a long time and continuing to reduce hexavalent chromium stably over a long period of time. Additionally, although polyphenols can be considered to have a potential to cause browning or discoloration because of their high reducing capacity, the above compounds are incorporated in leathers or leather articles before discoloration and are therefore less likely to cause color fading or color change, thus posing a lower risk of impairing the color or texture of leathers or leather articles. This is also the reason why the above compounds are preferred.

[0059] In formula (2) above, hydroxy groups are present at the 1-, 2-, and 3-positions. However, the same effect can be provided by compounds having a skeleton in which hydroxy groups are introduced at the 1-, 2-, and 4-positions (formula (5) above) or a skeleton in which hydroxy groups are introduced at the 1-, 3-, and 5-positions (formula (6) above). Derivatives of such compounds also have the same effect.

[0060] In formula (2) above, three hydroxy groups are introduced into one aromatic ring. However, compounds having one hydroxy group or two hydroxy groups on an aromatic ring also have the hexavalent chromium removing ability. Examples of compounds having such a skeleton include phenol, BHT, compounds represented by formulas (7), (8), and (9) above, and derivatives thereof.

[0061] Compounds having a hydroxy group on a plurality of linked aromatic rings also have the same effect. Examples of the compounds include those having one or more hydroxy groups on a naphthalene ring. Examples of such compounds having two hydroxy groups are those represented by formulas (10) and (11) above. Derivatives of such compounds also have the hexavalent chromium removing ability like the compounds previously described.

[0062] Compounds having one or more hydroxy groups introduced at any positions of an anthracene ring made up of three linked aromatic rings also exhibit the same ability. An example of such compounds is that represented by formula (12) above. Derivatives of such compounds also have the hexavalent chromium removing ability.

[0063] Examples of the compound represented by formula (1) include compounds having a long-chain alkyl group and a heterocyclic ring. Such compounds have enhanced organic nature and decreased water solubility. However, these compounds have improved affinity for organic solvents and thus have the advantage of being soluble in hydrocarbon solvents. An example of the compounds is that represented by formula (14) above.

[0064] Preferred as the compound represented by formula (1) above are catechins such as catechin, gallocatechin, catechin gallate, epicatechin, epigallocatechin, epicatechin gallate, epigallocatechin gallate, procyanidin, and theaflavin and derivatives of the catechins. These catechins are superior in terms of safety and exhibit high reducing power in leathers or leather articles.

(Organic Compound (B))

[0065] The organic compound (B) has the structure represented by formula (1) above and is devoid of, for example, the hydroxyphenyl group represented by formula (15). Being devoid of the hydroxyphenyl group, the organic compound (B) has difficulty in penetrating into leathers or leather articles; however, thanks to having the structure represented by formula (1), the organic compound (B) is capable of successfully detoxifying hexavalent chromium present at the surface of leathers or leather articles by reducing it into trivalent chromium. The use of the compound (B) can therefore provide an immediate effect on preventing hexavalent chromium ions from dissolving in a water-containing substance such as sweat or rain and leaching into the environment or contacting humans. An example of the organic compound (B) is a compound having a hetero ring. Examples of the hetero ring include furan, chromene, isochromene, and xanthene. Examples of derivatives of such compounds include the compound having the structure represented by formula (13) above and derivatives thereof, erythorbic acid and derivatives thereof, and 4-hydroxyfuran-2(5H)-one. These compounds have the hexavalent chromium removing ability.

[0066] Examples of the derivatives of ascorbic acid include, but are not limited to, ascorbic acid esters, ascorbic acid phosphate, ascorbic acid sulfate, ascorbyl glucoside (2-O-α-D-glucopyranosyl-L-ascorbic acid), ascorbyl glucosamine, and dehydroascorbic acid.

[0067] Examples of the derivatives of erythorbic acid include erythorbic acid esters.

[0068] In the present invention, the organic compound (B) is preferably at least one compound selected from ascorbic acid and erythorbic acid and is more preferably ascorbic acid. This compound is easily degradable, thus being unable to maintain its effect over a long period of time and likely to bleed out of leathers or leather articles. However, this compound has low irritation potential on, and is safe for, humans (skin) and, in addition, it has high reducing power and takes effect immediately. Bringing a simultaneous treatment agent containing the compound (B) into contact with a leather or leather article can therefore effectively prevent hexavalent chromium ions from leaching into the environment and contacting humans. In particular, the surface of the leather or leather article can be detoxified quickly, which makes it possible to successfully reduce the occurrence of skin roughness or allergy. The compound (B) is unreactive and incompatible with the organic compound (A) and undegradable by the compound (A). The compound (B) can therefore be well mixed in the simultaneous treatment agent. Additionally, when the compound (B) having strong reducing power is incorporated, browning or discoloration caused by the organic compound (A) can be prevented. The compound (B) is also preferred in that the compound (B), due to being easily degradable, is unlikely to cause coloring and does not impair the color or texture of leathers or leather articles.

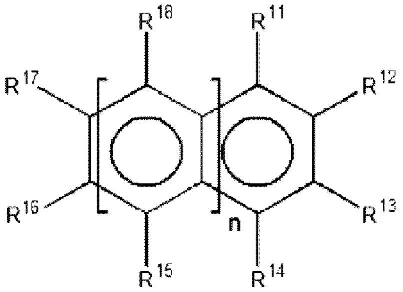
[0069] As stated above, compounds having the basic skeleton represented by formula (1) in the molecule are capable of detoxifying and removing hexavalent chromium.

(Preferred Embodiments of Hexavalent Chromium-Reducing Compound)

[0070] The hexavalent chromium-reducing compound is preferably at least one selected from a compound (A-i) represented by formula (A-i) below and a tannin (A-ii). It is more preferable to use the compound (A-i) represented by formula (A-i) below and the tannin (A-ii) in combination.

[0071] The compound (A-i) is represented by formula (A-i) below.

[Formula 16]

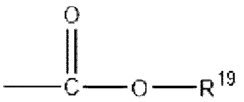


(A-i)

[0072] In the formula above, n represents 0, 1, or 2. That is, the compound (A-i) has a benzene, naphthalene, or anthracene structure.

[0073] R^{11} to R^{18} each independently represent a hydrogen atom, a hydroxy group, a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, or a group represented by formula (a-i) below. In formula (a-i), R^{19} is a C_1 to C_4 alkyl group.

[Formula 17]



$-C(=O)-O-R^{19}$

(a-i)

[0074] Examples of the C_1 to C_4 alkyl group include a methyl group, an ethyl group, a n-propyl group, an i-propyl group, a n-butyl group, an i-butyl group, a s-butyl group, and a t-butyl group. Examples of the C_1 to C_4 alkoxy group include a methoxy group, an ethoxy group, a n-propoxy group, an isopropoxy group, a n-butoxy group, an isobutoxy group, a s-butoxy group, and a t-butoxy group.

[0075] When n is 0, at least one of R^{11} to R^{14}, R^{16}, and R^{17} is a hydroxy group. It is preferable that two or three of R^{11} to R^{14}, R^{16}, and R^{17} be hydroxy groups, because in this case the ability to reduce hexavalent chromium is increased.

[0076] When n is 1 or 2, at least one of R^{11} to R^{18} is a hydroxy group. When n is 1 or 2, it is preferable that two or three of R^{11} to R^{18} be hydroxy groups, because in this case the ability to reduce hexavalent chromium is increased.

[0077] When n is 2, a plurality of R^{15} may be the same or different, and a plurality of R^{18} may be the same or different.

[0078] R^{16} and R^{17} may be linked together to form a five-membered ring or a six-membered ring. The atoms constituting the ring may include not only carbon atoms but also an oxygen atom. The ring may have a C_1 to C_{16} alkyl group as a substituent. The C_1 to C_{16} alkyl group may be linear or branched.

[0079] Specific examples of the compound (A-i) include the compounds represented by formulas (2), (3), (5) to (12), and (14) above and the compounds mentioned above as examples. One compound (A-i) may be used alone, or two or more compounds (A-i) may be used in combination.

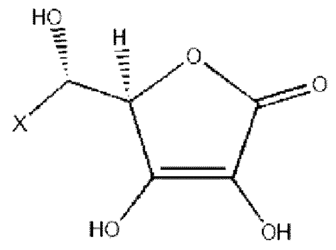
[0080] The tannin (A-ii) may be a hydrolyzable tannin or condensed tannin. Examples of the hydrolyzable tannin include gallotannins such as tannic acid (the compound represented by formula (4) above) and ellagitannin. In view of preparation of the simultaneous treatment agent described later, a hydrolyzable tannin is suitably used. One tannin (A-

ii) may be used, or two or more tannins (A-ii) may be used in combination.

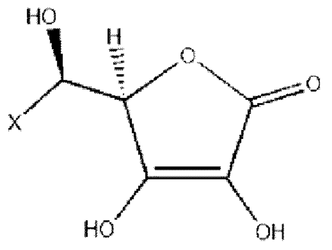
[0081] In the compound (A-i) and tannin (A-ii), the carbon to which a hydroxy group is bonded corresponds, for example, to the carbon 2 in formula (1) above.

[0082] The hexavalent chromium-reducing compound to be used preferably comprises at least one selected from a compound (B-i) represented by formula (B-i) below and a compound (B-ii) represented by formula (B-ii) below together with the compound (A-i) and tannin (A-ii).

[Formula 18]



(B-i)



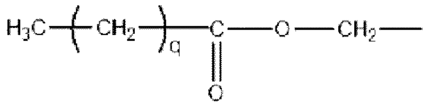
(B-ii)

[0083] In the formulas above, X is a group represented by any one of formulas (b-i) to (b-iii) below. In formulas (b-i) to (b-iii) below, o is an integer of 0 to 3, p is an integer of 1 to 3, and q is an integer of 1 to 17.

[Formula 19]

$$HO\left(CH_2\right)_o CH_2— \quad \text{(b-i)}$$

$$HO\left(CH_2O\right)_p CH_2— \quad \text{(b-ii)}$$



$$H_3C\left(CH_2\right)_q C(=O)—O—CH_2— \quad \text{(b-iii)}$$

[0084] Specific examples of the compound (B-i) and compound (B-ii) include the above compound represented by formula (13) and the compounds mentioned above as examples. One compound (B-i) may be used alone, or two or more compounds (B-i) may be used in combination. One compound (B-ii) may be used alone, or two or more compounds (B-ii) may be used in combination. The compounds (B-i) and (B-ii) may be used in combination.

[0085] When a leather is treated using the compound (A-i), (A-ii), (B-i), or (B-ii) as the hexavalent chromium-reducing compound, namely when a leather or leather article is treated so that the compound (A-i), (A-ii), (B-i), or (B-ii) is incorporated in the leather or leather article, not only hexavalent chromium having been present in the leather or leather article before the treatment but also hexavalent chromium produced by some cause after the treatment can be reduced, for example, into trivalent chromium which is non-toxic. This has the consequence that the hexavalent chromium content can be kept below the limit specified by Regulations (EU), No. 3014/2014 until the leather or leather article fulfills its function and purpose. In particular, when the compound (A-i) which takes effect immediately and the compound (A-ii) which takes effect slowly are combined, the hexavalent chromium content can be more reliably kept below the limit by the Regulations until the leather or leather article fulfills its function and purpose. When the compound (B-i) and/or (B-

ii) which has high reducing power and takes effect immediately is further combined with the compound (A-i) and/or (A-ii), hexavalent chromium, particularly that present in the vicinity of the surface of the leather or leather article, can be effectively reduced at the time of treatment.

[0086] When treatment with a hexavalent chromium-reducing compound is performed, specifically, a simultaneous treatment agent containing the hexavalent chromium-reducing compound is used. The proportions of the organic compounds (A) and (B) in the simultaneous treatment agent are not particularly limited as long as the effect of the present invention is obtained. The proportions are preferably such that the weight percentage ratio between the organic compounds (A) and (B) ((A):(B)) is 50 to 90:10 to 50, more preferably 50 to 80:20 to 50, and even more preferably 50 to 70:30 to 50 (it should be noted that the total amount of the compounds (A) and (B) is defined as 100% by weight). Although the organic compound (B) has a high ability to take effect immediately, it has difficulty in penetrating into leathers or leather articles and thus cannot have high long-term stability. The amount of the organic compound (B) is therefore preferably similar to or smaller than that of the organic compound (A). However, if the amount of the organic compound (B) is 10% by weight or less, there is a possibility that hexavalent chromium present in the surface of leathers or leather articles cannot be successfully reduced and detoxified into trivalent chromium.

[0087] When the simultaneous treatment agent comprises (i) the gallic acid ester, (ii) the at least one compound selected from tannic acid and a derivative thereof, and the organic compound (B), the proportions of these compounds are not particularly limited as long as the effect of the present invention is obtained. The proportions are preferably such that the weight percentage ratio ((i):(ii):(B)) is 1 to 20:30 to 89:10 to 50, more preferably 3 to 17:33 to 77:20 to 50, and even more preferably 5 to 15:35 to 65:30 to 50 (it should be noted that the total amount of the compounds (i), (ii), and (B) is defined as 100% by weight). The proportion of the organic compound (A) is as previously described. Preferred as the organic compound (B) is ascorbic acid and/or erythorbic acid, because ascorbic acid and erythorbic acid are incompatible with the compounds (i) and (ii) and are not incorporated in the compound (ii), thus being able to successfully reduce the surface of leathers or leather articles. The primary effect of the compounds (i) and (ii) is to reduce hexavalent chromium present inside leathers or leather articles. Ascorbic acid, propyl gallate, and tannic acid meet the international safety standards at concentrations thereof used in leather or leather articles regarding carcinogenicity, skin sensitization, and skin irritation as specified in the OECD Guidelines for the Testing of Chemicals. The compound (i) has high reducing power and is relatively easily degradable. The compound (ii) having a structural moiety corresponding to the compound (i) can be degraded to give the compound (i), and exhibits its reducing power more slowly than ascorbic acid and the gallic acid ester. The amount of the compound (ii) is therefore preferably greater than that of the compound (i). The compound (i) is pointed out as having somewhat higher potential to irritate humans (skin) than the compound (ii) and organic compound (B) and also has a relative risk of causing coloring. The amount of the compound (i) used is therefore preferably smaller than those of the compound (ii) and organic compound (B). If the amount of the compound (i) is less than 1% by weight, hexavalent chromium in leathers or leather articles may not be quickly detoxified, and hexavalent chromium ions remaining untreated may leach on the surface of leather or leather articles upon failure of the organic compound (B) to fully treat hexavalent chromium or after inactivation of the organic compound (B). Polyphenols can be considered to have a potential to cause browning or discoloration because of their high reducing capacity; however, when used in the above proportions, the compounds (i), (ii), and (B) can be successfully incorporated in leathers or leather articles before discoloration and are therefore less likely to cause color fading or color change, thus hardly impairing the color or texture of leathers or leather articles. This is a reason why the above proportions are preferred. The above proportions are preferred also because when used in the proportions, the compounds (i), (ii), and (B) are easily soluble both in water and in organic solvents. Such a simultaneous treatment agent is preferred because it can exhibit high long-term reliability.

[0088] When the simultaneous treatment agent comprises the compound (A-i) and the tannin (A-ii), the proportions of the compound (A-i) and the tannin (A-ii) are not particularly limited as long as the effect of the present invention is obtained. The proportions are preferably such that the weight percentage ratio ((A-i):(A-ii)) is 11 to 70:30 to 89, more preferably 23 to 67:33 to 77, and even more preferably 35 to 50:50 to 65 (it should be noted that the total amount of the compound (A-i) and tannin (A-ii) is defined as 100% by weight). With such proportions, the hexavalent chromium content can be kept low over a long period of time.

[0089] When the simultaneous treatment agent comprises the compound (A-i), the tannin (A-ii), and the compound (B-i) and/or(B-ii), the proportions of the compound (A-i), the tannin (A-ii), and the total of the compounds (B-i) and (B-ii) are not particularly limited as long as the effect of the present invention is obtained. The proportions are preferably such that the weight percentage ratio ((A-i):(A-ii) : (B-i) + (B-ii)) is 1 to 20:30 to 89:10 to 50, more preferably 3 to 17:33 to 77:20 to 50, and even more preferably 5 to 15:35 to 65:30 to 50 (it should be noted that the total amount of the compound (A-i), the tannin (A-ii), and the compounds (B-i) and (B-ii) is defined as 100% by weight). The reason why such proportions are preferred are as described above for the proportions of the compounds (i), (ii), and (B); namely, the compound (i), compound (ii), and compound (B) in the above description can be replaced by the compound (A-i), tannin (A-ii), and compounds (B-i) and (B-ii), respectively.

[Amounts of Components in Simultaneous Treatment Agent]

[0090] The amounts of the color material and oil contained with respect to 100% by mass of the simultaneous treatment agent are those in which they are used in ordinary cases. The hexavalent chromium-reducing compound is contained, for example, in an amount of 0.01 to 10.0% by mass with respect to 100% by mass of the simultaneous treatment agent.

[0091] When only the organic compound (A) is used as the hexavalent chromium-reducing compound, the total amount of the organic compound (A) contained in the simultaneous treatment agent is preferably, but not limited to, about 0.01 to 10.0% by weight, more preferably about 0.1 to 7.0% by weight, even more preferably about 0.3 to 5.0% by weight, still even more preferably about 0.5 to 3.0% by weight, and most preferably about 0.5 to 2.0% by weight, with respect to 100% by weight of the simultaneous treatment agent. The reason why this amount of the organic compound (A) is preferred is that in this case the potential to cause color fading or color change is particularly decreased. Additionally, the hexavalent chromium content can be kept low over a long period of time.

[0092] When the organic compounds (A) and (B) are used in combination, the total amount of the organic compounds (A) and (B) contained in the simultaneous treatment agent is preferably, but not limited to, about 0.01 to 10.0% by weight, more preferably about 0.1 to 7.0% by weight, even more preferably about 0.3 to 5.0% by weight, still even more preferably about 0.5 to 3.0% by weight, and most preferably about 0.5 to 2.0% by weight with respect to 100% by weight of the simultaneous treatment agent. The reason why this total amount of the organic compounds (A) and (B) is preferred that in this case the potential to cause color fading or color change is particularly decreased. Additionally, the hexavalent chromium content can be kept low over a long period of time.

[0093] When the simultaneous treatment agent comprises the compound (A-i) and/or tannin (A-ii) and optionally the compound (B-i) and/or compound (B-ii), the amounts of these compounds are as described above for the amounts of the compounds (A) and (B); namely, in the above description of the amounts of the components, the compound (A) can be replaced by the total of the compound (A-i) and tannin (A-ii), and the compound (B) can be replaced by the total of the compounds (B-i) and (B-ii).

[0094] The foregoing descriptions other than that of the amounts of the components also apply to the case where the simultaneous treatment agent comprises the compound (A-i) and/or tannin (A-ii) and optionally the compound (B-i) and/or compound (B-ii); namely, in the foregoing descriptions, the (i) gallic acid ester can be replaced by the compound (A-i), the (ii) tannic acid can be replaced by the compound (A-ii), the compound (A) can be replaced by the compound (A-i) and tannin (A-ii), and the compound (B) can be replaced by the compounds (B-i) and (B-ii).

[0095] The method for preparing the simultaneous treatment agent is not particularly limited as long as the above components can be dissolved. In order to dissolve the hexavalent chromium-reducing compound, for example, heating to 50 to 70°C is preferred.

[0096] In the dyeing-fatliquoring step and hexavalent chromium treatment step, the leather and simultaneous treatment agent are brought into contact. For example, the steps are carried out by placing the simultaneous treatment agent and the chrome-tanned leather together in a drum.

[0097] The proportions of the leather and simultaneous treatment agent can be those of a leather and a dyeing-fatliquoring agent in ordinary dyeing-fatliquoring. The conditions such as the treatment temperature and treatment time can be appropriately selected depending on the color material.

[0098] Through these steps, the leather is colored and endowed with properties such as flexibility.

[0099] Additionally, the hexavalent chromium-reducing compound having penetrated into the leather reduces hexavalent chromium present in the leather into trivalent chromium. Thus, the leather comes to contain trivalent chromium and the remaining hexavalent chromium-reducing compound not consumed in the reduction. Through the treatment with the hexavalent chromium-reducing compound, the hexavalent chromium content in the leather, as measured according to ISO 17075:2008-02, is typically decreased to less than 3 ppm, preferably to 2 ppm or less. The trivalent chromium content varies depending on the leather and is not particularly limited. The trivalent chromium content is typically 4000 ppm or more, and may be 4500 ppm or more or even 5000 ppm or more. The total chromium content remains unchanged before and after the treatment with the simultaneous treatment agent.

[0100] Once the hexavalent chromium-reducing compound is incorporated into a leather by the above treatment, the hexavalent chromium-reducing compound can, even when nontoxic chromium is converted to hexavalent chromium which is toxic after the treatment, detoxify the hexavalent chromium produced after the treatment. Therefore, the leather treated with the simultaneous treatment agent can keep the hexavalent chromium content below the limit specified by the Regulations until the leather or leather article fulfills its function and purpose.

[0101] In the method for producing a reptile leather according to the present invention, ordinary processes such as soaking, liming, deliming, pickling, splitting, shaving, and retanning may be performed as appropriate in addition to the steps described above.

<Other Embodiments>

[0102] Hereinafter, other embodiments will be described.

[0103] The method for producing a reptile leather according to the present invention is not limited to preferred embodiment [1] described above and may be implemented as embodiment [2] in which the hexavalent chromium treatment step is performed on the leather subjected to the chrome tanning in the chrome tanning step, the dyeing-fatliquoring step is then performed on the leather subjected to the hexavalent chromium treatment, and the finishing step is then performed on the leather subjected to the dyeing and fatliquoring. The method for producing a reptile leather according to the present invention may also be implemented as embodiment [3] in which the dyeing-fatliquoring step is performed on the leather subjected to the chrome tanning, the hexavalent chromium treatment step is then performed on the leather subjected to the dyeing and fatliquoring, and the finishing step is then performed on the leather subjected to the hexavalent chromium treatment.

[0104] In both of embodiments [2] and [3], the hexavalent chromium treatment step precedes the finishing step as in embodiment [1], and thus the leather's visual appearance obtained by the finishing step can be maintained without being impaired. Embodiment [1] is preferred in that the number of steps is smaller than those in embodiments [2] and [3]. If the dyeing-fatliquoring step is performed on the leather in a solvent after the hexavalent chromium treatment step, the hexavalent chromium-reducing compound incorporated in the leather may come out of the leather. Embodiments [1] and [3] are free of such a problem and preferred in this regard.

[0105] In embodiment [2], the hexavalent chromium treatment step is performed first. The hexavalent chromium treatment agent used in this step is preferably a treatment agent corresponding to the above simultaneous treatment agent from which the color material, oil, and surfactant are excluded (namely, a treatment agent containing the hexavalent chromium-reducing compound and water; this treatment agent may be referred to herein as a "hexavalent chromium-targeted treatment agent"). It should be noted that this treatment agent may contain a nonionic surfactant.

[0106] The solvent is not limited to water and may be a mixed solvent of water and an organic solvent. Examples of the organic solvent include C_1 to C_3 alcohols (methanol, ethanol, propanol, and isopropanol (IPA)), butanol, acetone, methyl ethyl ketone (MEK), and N,N-dimethylformamide (DMF).

[0107] To avoid impairing the texture of the leather, water alone or a mixed solvent of water and a C_1 to C_3 alcohol is preferably used, water alone or a mixed solvent of water and IPA is more preferably used, and water alone is even more preferably used. Since the hexavalent chromium treatment step in embodiment [2] is performed before fatliquoring, the treatment agent can easily penetrate into the leather even when the solvent is water.

[0108] When the solvent is a mixed solvent of water and an organic solvent, the amount of the organic solvent used is preferably more than 0% by mass and 20% by mass or less with respect to 100% by mass of the total amount of water and the organic solvent in order to avoid impairing the texture of the leather.

[0109] The leather treatment with the hexavalent chromium treatment agent described above, namely detoxification of hexavalent chromium, is carried out by bringing a leather containing hexavalent chromium into contact with the hexavalent chromium treatment agent. The method for making the contact is not particularly limited as long as the effect of the present invention is obtained. Examples of the method include spraying, atomizing, dipping, spreading, and immersion. Specifically, the treatment agent may be applied to the leather by spraying with a spray or by spreading with a brush. Alternatively, the surface of the leather may be rubbed with a cloth impregnated with the treatment agent. When a delicate leather such as a reptile leather which has a very vulnerable surface susceptible to scratches is treated, it is preferable to apply the agent to the leather by spraying with a spray. Since the hexavalent chromium treatment step in embodiment [2] is performed before fatliquoring, the treatment agent can easily penetrate into the leather both from the grain side of the leather and from the opposite side.

[0110] The amount of the hexavalent chromium treatment agent to be used can be determined as appropriate in consideration of the size and density of the fibers of the leather. To successfully accomplish the treatment with the hexavalent chromium treatment agent, it is preferable, for example, to apply the treatment agent containing the hexavalent chromium-reducing compound at a concentration within the range described above to one side of the to-be-treated surface of the leather using a spray, determine the amount of the applied treatment agent at the time when the treatment agent begins to seep to the other side of the to-be-treated surface of the leather, and employ the thus determined amount for the treatment. When this amount of the treatment agent is used, in general, the hexavalent chromium content can be kept below the limit specified by the Regulations until the leather or leather article fulfills its function and purpose. When the amount of the hexavalent chromium treatment agent to be used is determined in advance, it is preferable to use a leather whose properties such as the size and density of fibers are as close to those of the leather to be actually subjected to the hexavalent chromium treatment step as possible.

[0111] Next, the dyeing-fatliquoring step is performed by an ordinary method. The dyeing-fatliquoring agent used in this step is preferably a treatment agent corresponding to the above simultaneous treatment agent from which the hexavalent chromium-reducing compound is excluded (namely a treatment agent containing the color material, oil, surfactant, and water).

[0112] In embodiment [3], the dyeing-fatliquoring step is performed first by an ordinary method. The dyeing-fatliquoring agent used in this step is as described for embodiment [2].

[0113] Next, the hexavalent chromium treatment step is performed. The hexavalent chromium treatment agent used in this step is also as described for embodiment [2]. The method of treatment is also as described for embodiment [2]. However, since the hexavalent chromium treatment step in embodiment [3] is performed after fatliquoring, the solvent used is preferably a mixed solvent of water and an organic solvent, more preferably a mixed solvent of water and a C_1 to C_3 alcohol, and even more preferably a mixed solvent of water and IPA. The treatment agent penetrates into the leather more easily from the side opposite to the grain side than from the grain side, because the leather has been subjected to fatliquoring. It is therefore preferable to apply the treatment agent to the side of the leather opposite to the grain side.

[0114] The method for producing a reptile leather according to the present invention may be implemented as embodiment [1'] in which a simultaneous treatment agent containing water, a color material commonly used in dyeing of leathers, an oil prepared by solubilizing an oil commonly used in fatliquoring of leathers, and a hexavalent chromium-reducing compound is used instead of the simultaneous treatment agent used in embodiment [1]. The method for producing a reptile leather according to the present invention may be implemented as embodiment [2'] or [3'] in which a dyeing-fatliquoring agent containing water, a color material commonly used in dyeing of leathers, and an oil prepared by solubilizing an oil commonly used in fatliquoring of leathers is used instead of the dyeing-fatliquoring agent used in embodiment [2] or [3].

[0115] The method for producing a reptile leather according to the present invention is suitable also for use in production of fish leathers as well as in production of reptile leathers.

<Leather>

[0116] The reptile leather according to the present invention is a leather subjected to chrome tanning and comprises a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side, the hexavalent chromium-reducing compound being capable of reducing hexavalent chromium into trivalent chromium. The leather according to the present invention maintains the visual appearance as imparted by the finishing step. The leather according to the present invention is obtained, for example, by the above leather production method.

<Method for Producing Leather Article and Leather Article>

[0117] The method for producing a leather article according to the present invention comprises producing a leather by the above leather production method and further comprises a subsequent processing step of processing the leather. With the method for producing a leather article, the visual appearance as imparted to the leather by the finishing step in the course of production of the leather is maintained.

[0118] Examples of the leather article (processed leather product) include shoes, clothes, hats, gloves, belts, wallets, business card cases, watchbands, bags, book covers, pen cases, mobile phone cases, personal planners, key cases, glasses cases, and tool cases.

[0119] The processing step is performed by an ordinary method. Specifically, the leather article can be obtained by cutting a sheet of leather into a desired shape and attaching the cut sheet to a core material or the cut sheets to each other by means of an adhesive or by sewing. For example, a watchband is obtained as follows: a sheet of leather cut in the shape of the band is attached to the periphery, namely the front and back sides, of a core material with an adhesive, and the core material with the sheet of leather is heated. Depending on the type of the article, the article is finished, for example, by hemming for improving its texture.

[0120] The leather article according to the present invention comprises the leather described above. Examples of the leather article (processed leather product) are as mentioned above. In the leather article, the visual appearance as imparted to the leather by the finishing step in the course of production of the leather is maintained. The leather article according to the present invention is obtained, for example, by the above method for producing a leather article.

[0121] As described above, the present invention relates to the following.

> [1] A leather production method for producing a reptile leather, comprising: a chrome tanning step of performing chrome tanning on reptile skin to obtain a leather; a dyeing-fatliquoring step of performing dyeing and fatliquoring simultaneously on the leather subjected to the chrome tanning; and a finishing step of performing finishing on the leather subjected to the dyeing and fatliquoring,
> the method further comprising a hexavalent chromium treatment step of, prior to the finishing step, applying a hexavalent chromium-reducing compound capable of reducing hexavalent chromium into trivalent chromium to the leather subjected to the chrome tanning in the chrome tanning step.

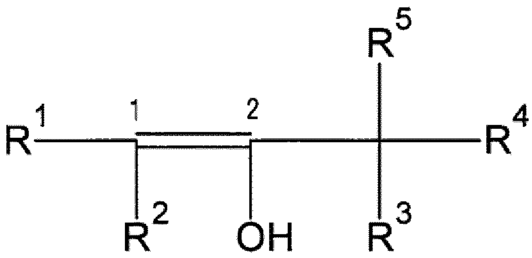
With the production method as defined above, a leather can be treated with a hexavalent chromium treatment agent in the course of leather production without change in the visual appearance of the leather.

[2] The leather production method for producing a reptile leather according to [1], wherein the dyeing-fatliquoring step and the hexavalent chromium treatment step are performed simultaneously on the leather subjected to the chrome tanning.

In the leather obtained as above, the visual appearance as imparted to the leather by the finishing step is maintained.

[3] The leather production method according to [1] or [2], wherein the hexavalent chromium-reducing compound is an organic compound (A) that has a structure represented by the following formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, that has a hydroxyphenyl group, and that has no aldehyde groups and no carboxyl groups:

[Formula 20]



$$R^1-C^1(R^2)=C^2(OH)-C(R^3)(R^4)(R^5)$$

· · · (1)

wherein R^1, R^2, R^3, R^4, and R^5 are each independently a substituent composed of C, H, O, and R^1 or R^2 and R^3, R^4, or R^5 may be linked together to form a ring.

[4] The leather production method according to [3], wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a dihydroxyphenyl group or a trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

[5] The leather production method according to [4], wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a 3,4,5-trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

[6] The leather production method according to [5], wherein the organic compound (A) comprises:

(i) a gallic acid ester; and
(ii) at least one compound selected from tannic acid and a derivative thereof.

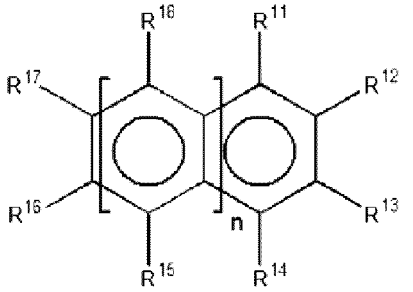
[7] The leather production method according to [6], wherein the compound (ii) is tannic acid.

[8] The leather production method according to any of [3] to [7], wherein the hexavalent chromium-reducing compound further comprises an organic compound (B) that has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium and that has no hydroxyphenyl groups, no aldehyde groups, and no carboxyl groups.

[9] The leather production method according to [8], wherein the organic compound (B) is at least one compound selected from ascorbic acid, a derivative of ascorbic acid, erythorbic acid, and a derivative of erythorbic acid.

[10] The leather production method according to [1] or [2], wherein the hexavalent chromium-reducing compound is at least one selected from a compound (A-i) represented by the following formula (A-i) and a tannin (A-ii):

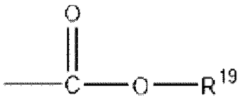
[Formula 21]



(A-i)

wherein
n represents 0, 1, or 2,
R^{11} to R^{18} each independently represent a hydrogen atom, a hydroxy group, a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, or a group represented by the following formula (a-i),
when n is 0, at least one of R^{11} to R^{14}, R^{16}, and R^{17} is a hydroxy group,
when n is 1 or 2, at least one of R^{11} to R^{18} is a hydroxy group,
when n is 2, a plurality of R^{15} may be the same or different, and a plurality of R^{18} may be the same or different,
R^{16} and R^{17} may be linked together to form a five-membered ring or a six-membered ring, and the ring may have a C_1 to C_{16} alkyl group as a substituent:

[Formula 22]

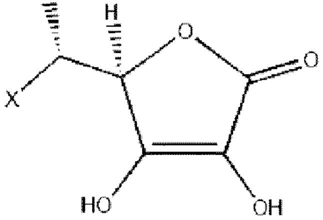


$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-R^{19}$$

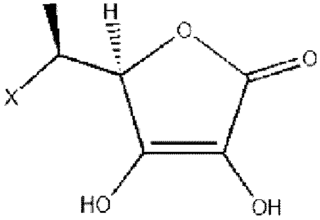
(a-i)

wherein R^{19} represents a C_1 to C_4 alkyl group.
[11] The leather production method according to [10], wherein the hexavalent chromium-reducing compound further comprises at least one selected from a compound (B-i) represented by the following formula (B-i) and a compound (B-ii) represented by the following formula (B-ii):

[Formula 23]



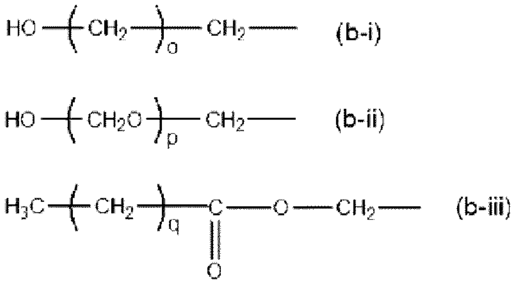
(B-i)



(B-ii)

wherein X represents a group represented by any one of the following formulas (b-i) to (b-iii):

[Formula 24]



$$HO{-}\left(CH_2\right)_o{-}CH_2{-} \quad \text{(b-i)}$$

$$HO{-}\left(CH_2O\right)_p{-}CH_2{-} \quad \text{(b-ii)}$$

$$H_3C{-}\left(CH_2\right)_q{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-} \quad \text{(b-iii)}$$

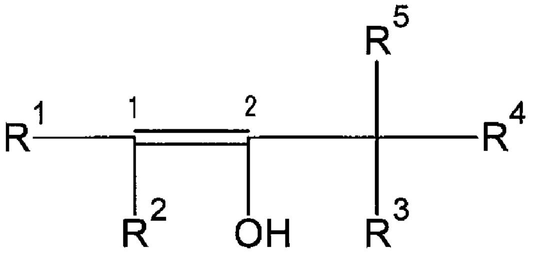
wherein o represents an integer of 0 to 3, p represents an integer of 1 to 3, and q represents an integer of 1 to 17. The use of any of the hexavalent chromium-reducing compounds as defined in [3] to [11] above enables a leather or leather article to keep the hexavalent chromium content below the limit specified by the Regulations (EU) No. 3014/2014 until the leather or leather article fulfills its function and purpose.

[12] A reptile leather subjected to chrome tanning, the leather comprising a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side, the hexavalent chromium-reducing compound being capable of reducing hexavalent chromium into trivalent chromium.

In the leather as defined above, the visual appearance as imparted to the leather by the finishing step is maintained.

[13] The leather according to [12], wherein the hexavalent chromium-reducing compound is an organic compound (A) that has a structure represented by the following formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, that has a hydroxyphenyl group, and that has no aldehyde groups and no carboxyl groups:

[Formula 25]



・・・(1)

R^1, R^2, R^3, R^4, and R^5 are each independently a substituent composed of C, H, O. R^1 or R^2 and R^3, R^4, or R^5 may be linked together to form a ring.

[14] The leather according to [13], wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a dihydroxyphenyl group or a trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

[15] The leather according to [14], wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a 3,4,5-trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

[16] The leather according to [15], wherein the organic compound (A) comprises:

(i) a gallic acid ester; and
(ii) at least one compound selected from tannic acid and a derivative thereof.

[17] The leather according to [16], wherein the compound (ii) is tannic acid.

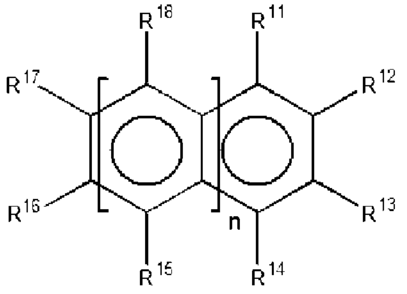
[18] The leather according to any one of [13] to [17], wherein the hexavalent chromium-reducing compound further comprises an organic compound (B) that has a structure represented by the formula (1) and capable of acting to

reduce hexavalent chromium into trivalent chromium and that has no hydroxyphenyl groups, no aldehyde groups, and no carboxyl groups.

[19] The leather according to [18], wherein the organic compound (B) is at least one compound selected from ascorbic acid, a derivative of ascorbic acid, erythorbic acid, and a derivative of erythorbic acid.

[20] The leather according to [12], wherein the hexavalent chromium-reducing compound is at least one selected from a compound (A-i) represented by the following formula (A-i) and a tannin (A-ii):

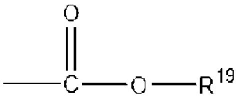
[Formula 26]



(A-i)

n represents 0, 1, or 2. R^{11} to R^{18} each independently represent a hydrogen atom, a hydroxy group, a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, or a group represented by the following formula (a-i) wherein R^{19} represents a C_1 to C_4 alkyl group. When n is 0, at least one of R^{11} to R^{14}, R^{16}, and R^{17} is a hydroxy group. When n is 1 or 2, at least one of R^{11} to R^{18} is a hydroxy group. When n is 2, a plurality of R^{15} may be the same or different, and a plurality of R^{18} may be the same or different. R^{16} and R^{17} may be linked together to form a five-membered ring or a six-membered ring, and the ring may have a C_1 to C_{16} alkyl group as a substituent.

[Formula 27]

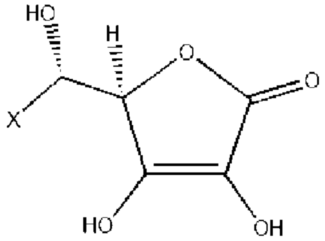


$$-C(=O)-O-R^{19}$$

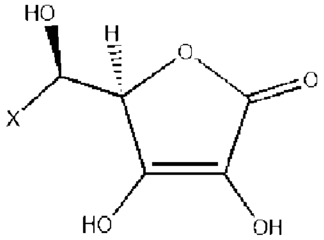
(a-i)

[21] The leather according to [20], wherein the hexavalent chromium-reducing compound further comprises at least one selected from a compound (B-i) represented by the following formula (B-i) and a compound (B-ii) represented by the following formula (B-ii):

[Formula 28]



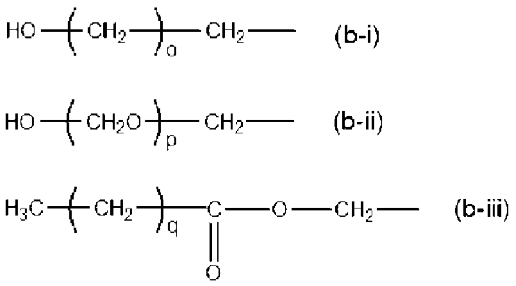
(B-i)



(B-ii)

X represents a group represented by any one of the following formulas (b-i) to (b-iii) wherein o represents an integer of 0 to 3, p represents an integer of 1 to 3, and q represents an integer of 1 to 17.

[Formula 29]



$$HO\text{—}(CH_2)_o\text{—}CH_2\text{—} \quad \text{(b-i)}$$

$$HO\text{—}(CH_2O)_p\text{—}CH_2\text{—} \quad \text{(b-ii)}$$

$$H_3C\text{—}(CH_2)_q\text{—}C(=O)\text{—}O\text{—}CH_2\text{—} \quad \text{(b-iii)}$$

The use of any of the hexavalent chromium-reducing compounds as defined in [13] to [21] above enables a leather or leather article to keep the hexavalent chromium content below the limit specified by the Regulations (EU) No. 3014/2014 until the leather or leather article fulfills its function and purpose.

[22] A method for producing a leather article, comprising producing a leather by the leather production method according to any one of [1] to [11], and further comprising a subsequent processing step of processing the leather.

[23] A leather article comprising the leather according to any one of [12] to [21].

[0122] With the above method for producing a leather article as defined above or in the leather article as defined above, the visual appearance as imparted to the leather by the finishing step is maintained.

[Examples]

[0123] Hereinafter, the present invention will be described in more detail with reference to examples. The present invention is not limited to these examples.

[Example 1-1]

[0124] A crocodile leather sheet (thickness: 1.5 mm) subjected to chrome tanning in the chrome tanning step was prepared. The hexavalent chromium content in this leather, as determined by the procedure according to ISO 17075:2008-02, was 8 ppm. The total chromium content was quantified with a fluorescent X-ray analyzer (an energy-dispersive fluorescent X-ray analyzer, "JSX-3202EV ELEMENT ANALYZER", available from JEOL Ltd.) and determined to be 7141 ppm. The reference samples used were JSX-3000 series reference sample 1, JSX-3000 series reference sample 2, and JSX-3000 series energy calibration reference sample which are available from JEOL Ltd. The measurement was conducted using JSX starter and then Plastic D3 in accordance with Quick Manual (Nos. EY07007-J00 and J00 EY07007G, issued in August 2007) provided by JEOL Ltd.

[0125] The dyeing-fatliquoring step and the hexavalent chromium treatment step were simultaneously performed on this leather as follows. A color material, an oil, a surfactant, 0.5 parts by weight of the compound represented by formula (3), 2.5 parts by weight of the compound represented by formula (4), and 2.0 parts by weight of the compound represented by formula (13) were mixed and dissolved in water to obtain a simultaneous treatment agent. The water was used in an amount such that the total amount of the treatment agent was 500 parts by weight.

[0126] The leather sheet and simultaneous treatment agent were placed in a drum, and the leather sheet was treated by rotating the drum.

[0127] After drying, a portion of the leather was cut out, and measured for the hexavalent chromium content according to ISO 17075:2008-02. The hexavalent chromium content was not more than the detection limit (2 ppm). The total chromium content as quantified by the fluorescent X-ray analyzer remained unchanged before and after the treatment with the hexavalent chromium treatment agent.

[0128] Another portion of the leather was tested using the below-described testing liquid with which hexavalent chromium-reducing compounds can be detected. It was thus confirmed that the leather contained a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side.

[0129] When a drop of the testing liquid is placed on a leather containing a hexavalent chromium-reducing compound, the testing liquid is colored blue. The greater the amount of the hexavalent chromium-reducing compound contained in the leather is, the more intensely the liquid is colored. A drop of the testing liquid was placed on samples shaved from the grain side in increments of 0.5 mm in the thickness direction, namely a sample shaved from the grain side to a depth of 0.5 mm and a sample shaved from a depth of 0.5 mm to a depth of 1.0 mm, and also on the remaining sample. The liquid was colored with the same level of intensity for all the samples.

(Testing Liquid)

[0130] Water and IPA were mixed in a ratio of 50:50 (weight percentage ratio) to prepare an aqueous solvent. 5 g of iron(III) chloride was dissolved in 95 g of the aqueous solvent to prepare a testing liquid containing iron(III) chloride in a concentration of 5% by mass.

[0131] The leather having undergone the dyeing-fatliquoring step and hexavalent chromium treatment step (the remaining portion of the above leather) was further subjected to glazing finish to obtain a glossy crocodile leather.

[Example 1-2]

[0132] A leather treated with a simultaneous treatment agent was obtained by performing the dyeing-fatliquoring step and hexavalent chromium treatment step simultaneously in the same manner as in Example 1-1, except for using 1.5 parts by weight of the compound represented by formula (3) and 3.5 parts by weight of the compound represented by formula (4) instead of 0.5 parts by weight of the compound represented by formula (3), 2.5 parts by weight of the compound represented by formula (4), and 2.0 parts by weight of the compound represented by formula (13).

[0133] After drying, a portion of the leather was cut out, and measured for the hexavalent chromium content according to ISO 17075:2008-02. The hexavalent chromium content was not more than the detection limit (2 ppm). The total chromium content as quantified by the fluorescent X-ray analyzer remained unchanged before and after the treatment with the hexavalent chromium treatment agent.

[0134] Another portion of the leather was tested using the above testing liquid. It was thus confirmed that the leather contained a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side. The test was conducted in the same manner as in Example 1-1.

[0135] The leather having undergone the dyeing-fatliquoring step and hexavalent chromium treatment step (the remaining portion of the above leather) was further subjected to glazing finish to obtain a glossy crocodile leather.

[Example 1-3]

[0136] A leather treated with a simultaneous treatment agent was obtained by performing the dyeing-fatliquoring step and hexavalent chromium treatment step simultaneously in the same manner as in Example 1-1, except for using 15 parts by weight of the compound represented by formula (4) instead of 0.5 parts by weight of the compound represented by formula (3), 2.5 parts by weight of the compound represented by formula (4), and 2.0 parts by weight of the compound represented by formula (13).

[0137] After drying, a portion of the leather was cut out, and measured for the hexavalent chromium content according to ISO 17075:2008-02. The hexavalent chromium content was not more than the detection limit (2 ppm). The total chromium content as quantified by the fluorescent X-ray analyzer remained unchanged before and after the treatment with the hexavalent chromium treatment agent.

[0138] Another portion of the leather was tested using the above testing liquid. It was thus confirmed that the leather contained a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side. The test was conducted in the same manner as in Example 1-1.

[0139] The leather having undergone the dyeing-fatliquoring step and hexavalent chromium treatment step (the remaining portion of the above leather) was further subjected to glazing finish to obtain a glossy crocodile leather.

[Example 2]

[0140] A crocodile leather sheet (thickness: 1.5 mm) subjected to chrome tanning in the chrome tanning step was prepared. The hexavalent chromium content in this leather, as determined by the procedure according to ISO 17075:2008-02, was 8 ppm. The total chromium content as quantified by the fluorescent X-ray analyzer was 7141 ppm.

[0141] The hexavalent chromium treatment step was performed on this leather as follows. 0.5 parts by weight of the compound represented by formula (3), 2.5 parts by weight of the compound represented by formula (4), and 2.0 parts by weight of the compound represented by formula (13) were mixed and dissolved in water to obtain a hexavalent chromium treatment agent. The water was used in an amount such that the total amount of the treatment agent was 500 parts by weight.

[0142] The above crocodile leather was immersed in the obtained treatment agent and then dried to obtain a hexavalent chromium treatment agent-treated leather.

[0143] Next, the dyeing-fatliquoring step was performed on the leather using a dyeing-fatliquoring agent containing a color material, an oil, and a surfactant.

[0144] After drying, a portion of the leather was cut out, and measured for the hexavalent chromium content according to ISO 17075:2008-02. The hexavalent chromium content was not more than the detection limit (2 ppm). The total chromium content as quantified by the fluorescent X-ray analyzer remained unchanged before and after the treatment with the hexavalent chromium treatment agent.

[0145] Another portion of the leather was tested using the above testing liquid. It was thus confirmed that the leather contained a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side. The test was conducted in the same manner as in Example 1-1.

[0146] The leather having undergone the dyeing-fatliquoring step and hexavalent chromium treatment step (the remaining portion of the above leather) was further subjected to glazing finish to obtain a glossy crocodile leather.

[Example 3]

[0147] A crocodile leather sheet (thickness: 1.5 mm) subjected to chrome tanning in the chrome tanning step was prepared. The hexavalent chromium content in this leather, as determined by the procedure according to ISO 17075:2008-02, was 8 ppm. The total chromium content was quantified with a fluorescent X-ray analyzer and determined to be 7141 ppm.

[0148] The dyeing-fatliquoring step was performed on this leather using a dyeing-fatliquoring agent containing a color material, an oil, and a surfactant.

[0149] Next, the hexavalent chromium treatment step was performed on the leather as follows. 0.5 parts by weight of the compound represented by formula (3), 2.5 parts by weight of the compound represented by formula (4), and 2.0 parts by weight of the compound represented by formula (13) were mixed and dissolved in a mixed solvent of water and IPA (50% by weight:50% by weight) to obtain a hexavalent chromium treatment agent. The mixed solvent was used in an amount such that the total amount of the treatment agent was 500 parts by weight.

[0150] The above crocodile leather was immersed in the obtained treatment agent and then dried to obtain a hexavalent chromium treatment agent-treated leather.

[0151] After drying, a portion of the leather was cut out, and measured for the hexavalent chromium content according to ISO 17075:2008-02. The hexavalent chromium content was not more than the detection limit (2 ppm). The total chromium content as quantified by the fluorescent X-ray analyzer remained unchanged before and after the treatment with the hexavalent chromium treatment agent.

[0152] Another portion of the leather was tested using the above testing liquid. It was thus confirmed that the leather contained a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side. The test was conducted in the same manner as in Example 1-1.

[0153] The leather having undergone the dyeing-fatliquoring step and hexavalent chromium treatment step (the remaining portion of the above leather) was further subjected to glazing finish to obtain a glossy crocodile leather.

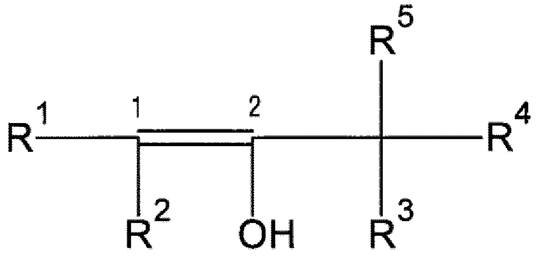
Claims

1. A leather production method for producing a reptile leather, comprising: a chrome tanning step of performing chrome tanning on reptile skin to obtain a leather; a dyeing-fatliquoring step of performing dyeing and fatliquoring simultaneously on the leather subjected to the chrome tanning; and a finishing step of performing finishing on the leather subjected to the dyeing and fatliquoring,
   the method further comprising a hexavalent chromium treatment step of, prior to the finishing step, applying a hexavalent chromium-reducing compound capable of reducing hexavalent chromium into trivalent chromium to the leather subjected to the chrome tanning in the chrome tanning step.

2. The leather production method according to claim 1, wherein the dyeing-fatliquoring step and the hexavalent chromium treatment step are performed simultaneously on the leather subjected to the chrome tanning.

3. The leather production method according to claim 1 or 2, wherein the hexavalent chromium-reducing compound is an organic compound (A) that has a structure represented by the following formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, that has a hydroxyphenyl group, and that has no aldehyde groups and no carboxyl groups:

[Formula 1]



. . . (1)

wherein R^1, R^2, R^3, R^4, and R^5 are each independently a substituent composed of C, H, O, and R^1 or R^2 and R^3, R^4, or R^5 may be linked together to form a ring.

4. The leather production method according to claim 3, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a dihydroxyphenyl group or a trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

5. The leather production method according to claim 4, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a 3,4,5-trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

6. The leather production method according to claim 5, wherein the organic compound (A) comprises:

   (i) a gallic acid ester; and
   (ii) at least one compound selected from tannic acid and a derivative thereof.

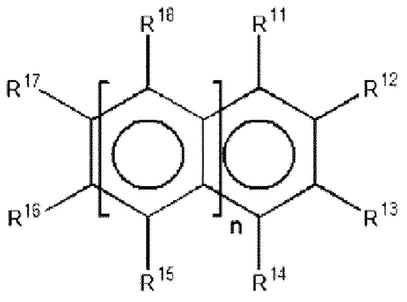
7. The leather production method according to claim 6, wherein the compound (ii) is tannic acid.

8. The leather production method according to any one of claims 3 to 7, wherein the hexavalent chromium-reducing compound further comprises an organic compound (B) that has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium and that has no hydroxyphenyl groups, no aldehyde groups, and no carboxyl groups.

9. The leather production method according to claim 8, wherein the organic compound (B) is at least one compound selected from ascorbic acid, a derivative of ascorbic acid, erythorbic acid, and a derivative of erythorbic acid.

10. The leather production method according to claim 1 or 2, wherein the hexavalent chromium-reducing compound is at least one selected from a compound (A-i) represented by the following formula (A-i) and a tannin (A-ii):

[Formula 2]

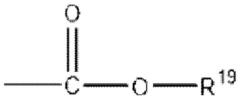


(A-i)

wherein
n represents 0, 1, or 2,

R^{11} to R^{18} each independently represent a hydrogen atom, a hydroxy group, a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, or a group represented by the following formula (a-i),
when n is 0, at least one of R^{11} to R^{14}, R^{16}, and R^{17} is a hydroxy group,
when n is 1 or 2, at least one of R^{11} to R^{18} is a hydroxy group,
when n is 2, a plurality of R^{15} may be the same or different, and a plurality of R^{18} may be the same or different,
R^{16} and R^{17} may be linked together to form a five-membered ring or a six-membered ring, and the ring may have a C_1 to C_{16} alkyl group as a substituent:

[Formula 3]



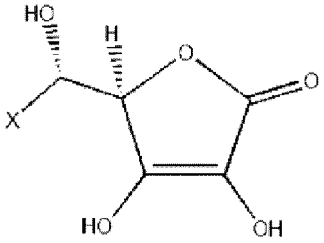
$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-R^{19}$$

(a-i)

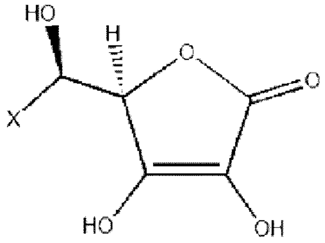
wherein R^{19} represents a C_1 to C_4 alkyl group.

11. The leather production method according to claim 10, wherein the hexavalent chromium-reducing compound further comprises at least one selected from a compound (B-i) represented by the following formula (B-i) and a compound (B-ii) represented by the following formula (B-ii):

[Formula 4]



(B-i)



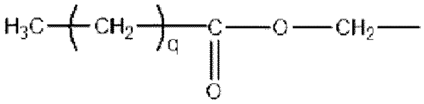
(B-ii)

wherein X represents a group represented by any one of the following formulas (b-i) to (b-iii):

[Formula 5]

$$HO-\left(CH_2\right)_o-CH_2- \quad \text{(b-i)}$$

$$HO-\left(CH_2O\right)_p-CH_2- \quad \text{(b-ii)}$$



$$H_3C-\left(CH_2\right)_q-\underset{\underset{\displaystyle O}{\|}}{C}-O-CH_2-$$

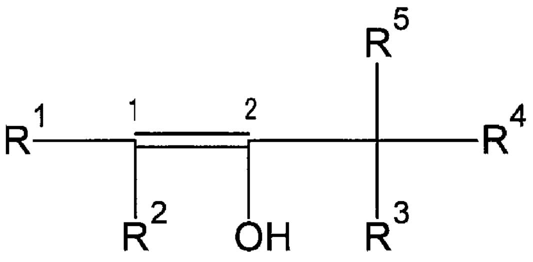
(b-iii)

wherein o represents an integer of 0 to 3, p represents an integer of 1 to 3, and q represents an integer of 1 to 17.

12. A reptile leather subjected to chrome tanning, the leather comprising a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side, the hexavalent chromium-reducing compound being capable of reducing hexavalent chromium into trivalent chromium.

13. The leather according to claim 12, wherein the hexavalent chromium-reducing compound is an organic compound (A) that has a structure represented by the following formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, that has a hydroxyphenyl group, and that has no aldehyde groups and no carboxyl groups:

[Formula 6]



... (1)

wherein R^1, R^2, R^3, R^4, and R^5 are each independently a substituent composed of C, H, O, and R^1 or R^2 and R^3, R^4, or R^5 may be linked together to form a ring.

14. The leather according to claim 13, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a dihydroxyphenyl group or a trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

15. The leather according to claim 14, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a 3,4,5-trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

16. The leather according to claim 15, wherein the organic compound (A) comprises:

(i) a gallic acid ester; and
(ii) at least one compound selected from tannic acid and a derivative thereof.

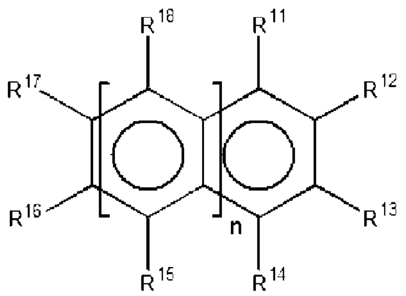
17. The leather according to claim 16, wherein the compound (ii) is tannic acid.

18. The leather according to any one of claims 13 to 17, wherein the hexavalent chromium-reducing compound further comprises an organic compound (B) that has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium and that has no hydroxyphenyl groups, no aldehyde groups, and no carboxyl groups.

19. The leather according to claim 18, wherein the organic compound (B) is at least one compound selected from ascorbic acid, a derivative of ascorbic acid, erythorbic acid, and a derivative of erythorbic acid.

20. The leather according to claim 12, wherein the hexavalent chromium-reducing compound is at least one selected from a compound (A-i) represented by the following formula (A-i) and a tannin (A-ii):

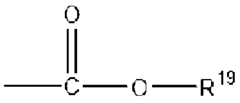
[Formula 7]



(A-i)

wherein
n represents 0, 1, or 2,
R^{11} to R^{18} each independently represent a hydrogen atom, a hydroxy group, a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, or a group represented by the following formula (a-i),
when n is 0, at least one of R^{11} to R^{14}, R^{16}, and R^{17} is a hydroxy group,
when n is 1 or 2, at least one of R^{11} to R^{18} is a hydroxy group,
when n is 2, a plurality of R^{15} may be the same or different, and a plurality of R^{18} may be the same or different,
R^{16} and R^{17} may be linked together to form a five-membered ring or a six-membered ring, and the ring may have a C_1 to C_{16} alkyl group as a substituent:

[Formula 8]



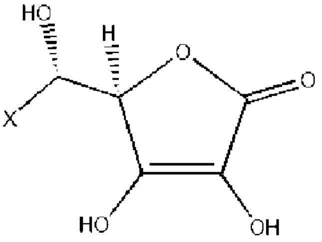
$$-C(=O)-O-R^{19}$$

(a-i)

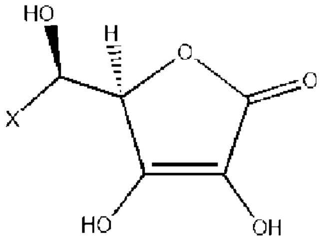
wherein R^{19} represents a C_1 to C_4 alkyl group.

21. The leather according to claim 20, wherein the hexavalent chromium-reducing compound further comprises at least one selected from a compound (B-i) represented by the following formula (B-i) and a compound (B-ii) represented by the following formula (B-ii):

[Formula 9]



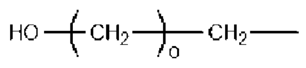
(B-i)



(B-ii)

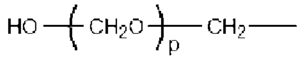
wherein X represents a group represented by any one of the following formulas (b-i) to (b-iii):

[Formula 10]



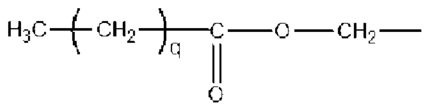
$$HO-(CH_2)_o-CH_2-$$

(b-i)



$$HO-(CH_2O)_p-CH_2-$$

(b-ii)



$$H_3C-(CH_2)_q-C(=O)-O-CH_2-$$

(b-iii)

wherein o represents an integer of 0 to 3, p represents an integer of 1 to 3, and q represents an integer of 1 to 17.

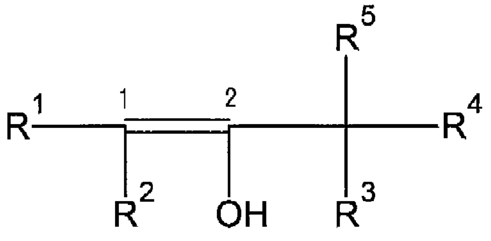
22. A method for producing a leather article, comprising producing a leather by the leather production method according to any one of claims 1 to 11, and further comprising a subsequent processing step of processing the leather.

23. A leather article comprising the leather according to any one of claims 12 to 21.

Amended claims under Art. 19.1 PCT

1. (Amended) A leather production method for producing a reptile leather, comprising: a chrome tanning step of performing chrome tanning on reptile skin to obtain a leather; a dyeing-fatliquoring step of performing dyeing and fatliquoring simultaneously on the leather subjected to the chrome tanning; and a finishing step of performing finishing on the leather subjected to the dyeing and fatliquoring,
the method further comprising a hexavalent chromium treatment step of, prior to the finishing step, applying a hexavalent chromium-reducing compound capable of reducing hexavalent chromium into trivalent chromium to the leather subjected to the chrome tanning in the chrome tanning step,
wherein the hexavalent chromium-reducing compound is an organic compound (A) that has a structure represented by the following formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, that has a hydroxyphenyl group, and that has no aldehyde groups and no carboxyl groups:

[Formula 1]



· · · (1)

wherein R^1, R^2, R^3, R^4, and R^5 are each independently a substituent composed of C, H, O, and R^1 or R^2 and R^3, R^4, or R^5 may be linked together to form a ring.

2. The leather production method according to claim 1, wherein the dyeing-fatliquoring step and the hexavalent chromium treatment step are performed simultaneously on the leather subjected to the chrome tanning.

3. (Amended) The leather production method according to claim 1, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a dihydroxyphenyl group or a trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

4. (Amended) The leather production method according to claim 3, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a 3,4,5-trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

5. (Amended) The leather production method according to claim 4, wherein the organic compound (A) comprises:

   (i) a gallic acid ester; and
   (ii) at least one compound selected from tannic acid and a derivative thereof.

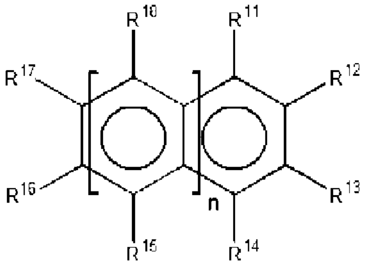
6. (Amended) The leather production method according to claim 5, wherein the compound (ii) is tannic acid.

7. (Amended) The leather production method according to any one of claims 1 to 6, wherein the hexavalent chromium-reducing compound further comprises an organic compound (B) that has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium and that has no hydroxyphenyl groups, no aldehyde groups, and no carboxyl groups.

8. (Amended) The leather production method according to claim 7, wherein the organic compound (B) is at least one compound selected from ascorbic acid, a derivative of ascorbic acid, erythorbic acid, and a derivative of erythorbic acid.

9. (Amended) The leather production method according to claim 1 or 2, wherein the hexavalent chromium-reducing compound is at least one selected from a compound (A-i) represented by the following formula (A-i) and a tannin (A-ii):

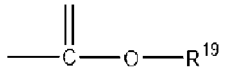
[Formula 2]



(A-i)

wherein
n represents 0, 1, or 2,
R^{11} to R^{18} each independently represent a hydrogen atom, a hydroxy group, a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, or a group represented by the following formula (a-i),
when n is 0, at least one of R^{11} to R^{14}, R^{16}, and R^{17} is a hydroxy group,
when n is 1 or 2, at least one of R^{11} to R^{18} is a hydroxy group,
when n is 2, a plurality of R^{15} may be the same or different, and a plurality of R^{18} may be the same or different,
R^{16} and R^{17} may be linked together to form a five-membered ring or a six-membered ring, and the ring may have a C_1 to C_{16} alkyl group as a substituent:

[Formula 3]



$$—\overset{\displaystyle O}{\overset{\|}{C}}—O—R^{19}$$

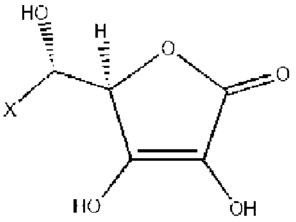
(a-i)

wherein R^{19} represents a C_1 to C_4 alkyl group.

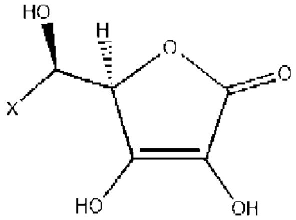
10. (Amended) The leather production method according to claim 9, wherein the hexavalent chromium-reducing compound further comprises at least one selected from a compound (B-i) represented by the following formula (B-i) and

a compound (B-ii) represented by the following formula (B-ii):

[Formula 4]



(B-i)



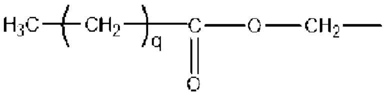
(B-ii)

wherein X represents a group represented by any one of the following formulas (b-i) to (b-iii):

[Formula 5]

$$\mathrm{HO}\left(\mathrm{CH_2}\right)_o\mathrm{CH_2}-$$ (b-i)

$$\mathrm{HO}\left(\mathrm{CH_2O}\right)_p\mathrm{CH_2}-$$ (b-ii)



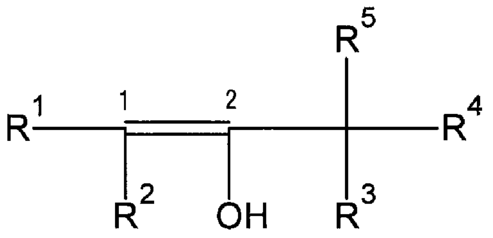
$$\mathrm{H_3C}\left(\mathrm{CH_2}\right)_q\mathrm{C(=O)}-\mathrm{O}-\mathrm{CH_2}-$$ (b-iii)

wherein o represents an integer of 0 to 3, p represents an integer of 1 to 3, and q represents an integer of 1 to 17.

11. (Amended) A reptile leather subjected to chrome tanning, the leather comprising a hexavalent chromium-reducing compound without a concentration gradient from the grain side of the leather to the opposite side, the hexavalent chromium-reducing compound being capable of reducing hexavalent chromium into trivalent chromium.

12. (Amended) The leather according to claim 11, wherein the hexavalent chromium-reducing compound is an organic compound (A) that has a structure represented by the following formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, that has a hydroxyphenyl group, and that has no aldehyde groups and no carboxyl groups:

[Formula 6]



· · · (1)

wherein R^1, R^2, R^3, R^4, and R^5 are each independently a substituent composed of C, H, O, and R^1 or R^2 and R^3, R^4, or R^5 may be linked together to form a ring.

13. (Amended) The leather according to claim 12, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a dihydroxyphenyl group or a trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

14. (Amended) The leather according to claim 13, wherein the organic compound (A) has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium, has a 3,4,5-trihydroxyphenyl group, and has no aldehyde groups and no carboxyl groups.

15. (Amended) The leather according to claim 14, wherein the organic compound (A) comprises:

(i) a gallic acid ester; and
(ii) at least one compound selected from tannic acid and a derivative thereof.

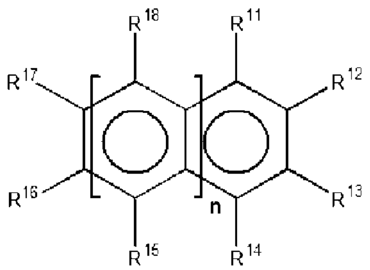
16. (Amended) The leather according to claim 15, wherein the compound (ii) is tannic acid.

17. (Amended) The leather according to any one of claims 12 to 16, wherein the hexavalent chromium-reducing compound further comprises an organic compound (B) that has a structure represented by the formula (1) and capable of acting to reduce hexavalent chromium into trivalent chromium and that has no hydroxyphenyl groups, no aldehyde groups, and no carboxyl groups.

18. (Amended) The leather according to claim 17, wherein the organic compound (B) is at least one compound selected from ascorbic acid, a derivative of ascorbic acid, erythorbic acid, and a derivative of erythorbic acid.

19. (Amended) The leather according to claim 11, wherein the hexavalent chromium-reducing compound is at least one selected from a compound (A-i) represented by the following formula (A-i) and a tannin (A-ii):

[Formula 7]

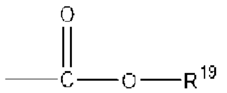


(A-i)

wherein
n represents 0, 1, or 2,
R^{11} to R^{18} each independently represent a hydrogen atom, a hydroxy group, a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, or a group represented by the following formula (a-i),
when n is 0, at least one of R^{11} to R^{14}, R^{16}, and R^{17} is a hydroxy group,
when n is 1 or 2, at least one of R^{11} to R^{18} is a hydroxy group,

when n is 2, a plurality of R^{15} may be the same or different, and a plurality of R^{18} may be the same or different, R^{16} and R^{17} may be linked together to form a five-membered ring or a six-membered ring, and the ring may have a C_1 to C_{16} alkyl group as a substituent:

[Formula 8]

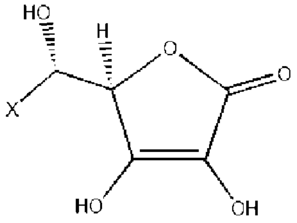


$$-C(=O)-O-R^{19} \quad \text{(a-i)}$$

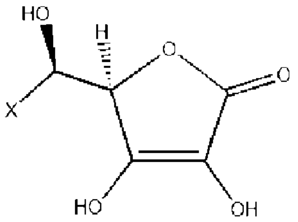
wherein R^{19} represents a C_1 to C_4 alkyl group.

20. (Amended) The leather according to claim 19, wherein the hexavalent chromium-reducing compound further comprises at least one selected from a compound (B-i) represented by the following formula (B-i) and a compound (B-ii) represented by the following formula (B-ii):

[Formula 9]



(B-i)



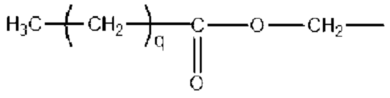
(B-ii)

wherein X represents a group represented by any one of the following formulas (b-i) to (b-iii):

[Formula 10]

$$HO\left(CH_2\right)_o CH_2- \quad \text{(b-i)}$$

$$HO\left(CH_2O\right)_p CH_2- \quad \text{(b-ii)}$$



$$H_3C\left(CH_2\right)_q C(=O)-O-CH_2- \quad \text{(b-iii)}$$

wherein o represents an integer of 0 to 3, p represents an integer of 1 to 3, and q represents an integer of 1 to 17.

21. (Amended) A method for producing a leather article, comprising producing a leather by the leather production method according to any one of claims 1 to 10, and further comprising a subsequent processing step of processing the leather.

22. (Amended) A leather article comprising the leather according to any one of claims 11 to 20.

23. (Canceled)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/002891

A. CLASSIFICATION OF SUBJECT MATTER
C14C3/06(2006.01)i, *D06P3/32*(2006.01)i, *D06P5/00*(2006.01)i

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)
B68F1/00-3/04, C14B1/00-99/00, C14C1/00-99/00, D06P1/00-1/673, D06P1/90, D06P3/00-5/22, D06P7/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Japio-GPG/FX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/061945 A1 (Midori Hokuyo Co., Ltd.), 26 May 2011 (26.05.2011), claims 1 to 3; paragraph [0027]	1-5,10, 12-15,20,22, 23
A	& US 2012/0231249 A1 claims 1 to 3; paragraph [0131] & CN 102782160 A	6-9,11, 16-19,21
Y	WO 2014/112404 A1 (Kyohshin Co., Ltd.), 24 July 2014 (24.07.2014), paragraph [0018]	1-5,10, 12-15,20,22, 23
A	(Family: none)	6-9,11, 16-19,21

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

* Special categories of cited documents:
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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
“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“&” document member of the same patent family

Date of the actual completion of the international search
13 April 2017 (13.04.17)

Date of mailing of the international search report
25 April 2017 (25.04.17)

Name and mailing address of the ISA/
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Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/002891

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	KR 10-2012-0125032 A (KEUN DAE ENTERPRISE CO., LTD.), 14 November 2012 (14.11.2012), claim 1; examples (Family: none)	1,2,22 3-21,23
A	CN 103374634 A (XIANYANG GALAXY INORGANIC MATERIALS CO., LTD.), 30 October 2013 (30.10.2013), abstract; claim 1 (Family: none)	1-23
E,X E,A	JP 2017-039876 A (Japan Institute of Leather Research), 23 February 2017 (23.02.2017), claims 1, 6; paragraphs [0002], [0038], [0039] (Family: none)	1,3-5,8-15,18-23 2,6,7,16,17

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2015071509 W **[0027]**

Non-patent literature cited in the description

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- JSX-3202EV ELEMENT ANALYZER. X-ray analyzer. JEOL Ltd, **[0124]**
- Quick Manual. JEOL Ltd, August 2007 **[0124]**