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(54) Title: TREATMENT OF TEXTILE MATERIAL

(57) Abstract: The present invention generally relates to a method for increasing the color of a dyed textile material comprising the steps of: a) pretreating the textile material with at least one nitrate salt and an acid catalyst, b) drying the pretreated fabric in a dryer at temperatures less than 60 °C, c) applying a laser beam to the fabric to promote the chemical reaction to generate NO_x compounds which attach the dye, and d) creating a color value change.



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TREATMENT OF TEXTILE MATERIAL

Description

Field of the Invention

[0001] The present invention relates to non hazardous methods to improve the treatment of a fabric and specifically to increase the abrasion intensity of laser treated fabric.

Background Art

[0002] Fabric, such as denim, can be processed to simulate a worn look.

Conventionally, a wet process such as a stone and/or enzyme process are applied to the fabric, typically after the fabric has been transformed into a garment, to create a faded and/or worn look. Specifically, an enzyme wash in combination with an agitation element, such as stones or rocks, removes color from a ridged blue denim fabric to develop a contrasting pattern of variable color intensities creating a stonewashed look. In an exemplary embodiment, the faded areas of the denim fabric can correspond to where stones or rocks contact the fabric during the enzyme washing process.

[0003] However, traditional stonewash and/or enzyme processes have numerous drawbacks. For example, it is difficult to direct the abrasive action to specific parts of the garment (i.e. knees, bottom, etc.) and each manufacturing cycle requires extensive time to create the stonewashed look, where a significant amount of water is used during the process. In addition, potassium permanganate is widely used to create localized abrasion effects. The handling and disposal of the spray solution as well as the accrued wastewater require substantial attention regarding environmental concerns.

[0004] A CO₂ laser treatment has been used for several years for surface designing of patterns. The CO₂ laser treatment is a dry treatment and can be applied to textile materials as an alternative to conventional dry and wet treatments such as hand sanding, sand blasting, stone washing and bleaching, for achieving faded look and worn out effects.

[0005] US 5,567,207 discloses a method for making and fading textile with lasers. The laser is used to simulate conventional laundering techniques, such as stone washing, ball washing and acid washing, without the use of water or chemicals. The laser burns the surface of the denim fabric. Depending on the intensity of the laser every color from blue or black to complete white can be achieved. The lighter the

bleaching effect is, the more dramatic is the fiber damage, which can cause breaking of the fabric.

[0006] US 6,819,972 discloses a laser method to simulate the abrasion effect of a worn look. The patent teaches to define a desired pattern of color alterations to be formed on a garment by selecting a plurality of areas on a display and to associate a level of abrasion with each area. The patent further teaches to change the energy density per unit time along a single scan line in order to achieve the feathering required to simulate the worn look. Lasers operating in this fashion can simulate the worn look, but the garments often need to be processed after the laser treatment with hand sanding and/or potassium permanganate in order to improve abrasion intensity and pattern characteristics. Further, to achieve the worn look on a pair of jeans, the laser time may exceed several minutes with a conventional 100 - 200 watt laser in order to achieve the required energy intensity. Higher power lasers from 500 to 2,500 watts can on the one hand significantly reduce the time, but on the other hand require larger capital investments.

[0007] Currently one leading company in the laser treatment of textiles offers a process to laser abrade the worn look pattern on the jean twice. Once at the beginning of the wash cycle, followed by washing and drying of the garment, and then again laser abrasion of the previous worn look pattern on the washed garment in order to increase the abrasion effect and gain the desired intensity

[0008] Hence there is a critical need for inventive means to solve the industry wide environmental issue to create the worn out looks without the use of potassium permanganate.

Summary of invention

[0009] According the invention there is provided a method for changing the color of a fiber, yarn, fabric or garment in order to obtain a vintage look, wherein said fiber, yarn, fabric or garment is subjected to a treatment with a nitrogen salt in presence of an acid catalyst or treatment conditions which induce acid formation.

[0010] Specifically, the present invention relates to a method for increasing the color of a dyed textile material comprising the steps of:

- a. pretreating the textile material with at least one nitrate salt and an acid catalyst,
- b. drying the pretreated fabric in a dryer at temperatures less than 60 °C,

- c. applying a laser beam to the fabric to promote the chemical reaction to generate NO_x compounds which attack the dye, and
- d. thereby creating a color value change.

[0011] A further embodiment of the invention relates to a method as described above, wherein the nitrate salt is an organic or inorganic nitrate salt.

[0012] A further embodiment of the invention relates to the method as described above, wherein the inorganic nitrate salt is selected from the group consisting of $\text{Mg}(\text{NO}_3)_2$, KNO_3 , LiNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, NaNO_3 , RbNO_3 , CsNO_3 , $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sc}(\text{NO}_3)_3$, $\text{Ti}(\text{NO}_3)_4$, $\text{Zr}(\text{NO}_3)_4$, $\text{VO}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$, AgNO_3 , $\text{Cd}(\text{NO}_3)_2$, $\text{Hg}_2(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $[\text{B}(\text{NO}_3)_4]^-$, $\text{Ga}(\text{NO}_3)_3$, $\text{Tl}(\text{NO}_3)_3$, $\text{Pb}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, FNO_3 , ClNO_3 , $\text{Xe}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_4$, $\text{Gd}(\text{NO}_3)_3$.

[0013] A further embodiment of the invention relates to the method as described above, wherein nitrate salt is $\text{Mg}(\text{NO}_3)_2$, KNO_3 , LiNO_3 , NaNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

[0014] A further embodiment of the invention relates to the method as described above, wherein the nitrate salt is applied in solution, wet or dry form.

[0015] A further embodiment of the invention relates to the method as described above, wherein the acid catalyst is selected from the group consisting of organic or inorganic compounds, i.e. organic or inorganic chlorides, sulfates, phosphates, borates, fluorides, acid forming esters, amino acid hydrochlorides, and Lewis acid chlorides.

[0016] A further embodiment of the invention relates to the method as described above, wherein the nitrate salt is applied on local parts of the fabric.

[0017] A further embodiment of the invention relates to the method as described above, wherein the nitrate salt is applied on local parts of the fabric in a way whereupon figurative patterns are obtained.

[0018] A further embodiment of the invention relates to the method as described above, wherein the acid catalyst is selected from the group consisting of methanesulfonic acid, citric acid, tartaric acid, oxalic acid, toluenesulfonic acid, succinic acid, maleic acid, malic acid, sulfuric acid, hydrochloric acid, phosphoric acid, salicylic acid and mixtures thereof.

[0019] A further embodiment of the invention relates to the method as described above, wherein the Lewis acid chloride is ferric chloride, zinc chloride, lithium chloride, copper chloride, magnesium chloride or aluminum chloride and a sulfate as magnesium sulfate, iron sulfate, iron sulfate, cerium sulfate, vanadium sulfate, copper sulfate, lithium sulfate, aluminum sulfate, potassium aluminum sulfate, ammonium aluminum sulfate, sodium sulfate, sodium hydrogen sulfate, zinc sulfate and manganese sulfate, and the phosphate is a monosodium phosphate, disodium phosphate, monopotassium phosphate, dipotassium phosphate, monomagnesium phosphate, dimagnesium phosphate, trimagnesium phosphate, ammonium polyphosphate, monoammonium phosphate, diammonium phosphate, monocalcium phosphate, dicalcium phosphate, disodium pyrophosphate, trisodium pyrophosphate, tetrasodium pyrophosphate, sodium triphosphate, pentapotassium triphosphate.

[0020] A further embodiment of the invention relates to the method as described above, wherein the acid catalyst is provided as a buffered substance.

[0021] A further embodiment of the invention relates to the method as described above, wherein the acid catalyst is capsuled.

[0022] A further embodiment of the invention relates to the method as described above, wherein the treatment is carried out by a temperature of below 65 °C, or at a temperature of below 90 °C, or at higher temperature where applicable, if the acid catalyst decreases the activation temperature in comparison to the pure nitrate compound.

[0023] A further embodiment of the invention relates to the method as described above, wherein the aqueous solution comprises $\text{Mg}(\text{NO}_3)_2$, optionally another nitrate compound (e.g. $\text{Al}(\text{NO}_3)_3$) and an acid, e.g. tartaric acid.

[0024] A further embodiment of the invention relates to the method as described above, wherein the aqueous solution comprises $\text{Al}(\text{NO}_3)_3$ and toluenesulfonic acid.

[0025] A further embodiment of the invention relates to the method as described above, wherein the pH of the aqueous solution is higher than 2.

[0026] A further embodiment of the invention relates to the method as described above, wherein the pretreatment is carried out at a temperature of about 10 to 90 °C, or at a temperature of about 10 to 60 °C, or at a temperature of about 10 to 50 °C or at room temperature.

[0027] A further embodiment of the invention relates to the method as described above, wherein the pretreatment step is carried out in the presence of a sulfate and/or chloride compound.

[0028] A further embodiment of the invention relates to the method as described above, wherein optionally an auxiliary agent is used.

[0029] A further embodiment of the invention relates to the method as described above, wherein the auxiliary agent is present in an amount of 0.01-15 vol%.

[0030] A further embodiment of the invention relates to the method as described above, wherein the auxiliary agent is selected from the group consisting of another nitrate, softener, brightening agent, plastic, natural and synthetic polymers, silicates, silica, a thickening agent, dyestuff used as a marker dye, a wetting agent, a complexing agent, a dispersing agent, and a buffer solution derived from the salt of an acid and the corresponding acid.

[0031] A further embodiment of the invention relates to the method as described above, wherein the fabric is dyed with a sulphur dye, reactive dye, direct dye, VAT dye, basic dye, pigment dye, or natural dye or a mixture thereof.

[0032] A further embodiment of the invention relates to the method as described above, wherein the fabric is indigo dyed.

[0033] A further embodiment of the invention relates to the method as described above, wherein wherein the ΔL value between the untreated and treated part is greater than 2 (L stands for the lightness in the CIE 1976 Lab color space).

[0034] A further embodiment of the invention relates to the method as described above, wherein the laser beam is applied to the fabric to change the color intensity to value ranges of L from 15-40 to 30-60, or from 15-30 to 30-60.

[0035] A further embodiment of the invention relates to the method as described above, wherein the Lab color space lightness value ranges for L of from 20 to 60 are achieved by laser treatment.

[0036] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by mixing a nitrate salt with a buffer compound containing a phosphoric acid and corresponding salts of this acid, applying this solution to a fabric, drying the fabric in a dryer by selecting the temperature in such a way that the bleaching reaction does not take place in a significant way during the drying step (e.g.

less than 60 °C), and applying a laser beam to the fabric to generate nitrogen oxide compounds, which attack the indigo dye and thereby create a color value change.

[0037] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by mixing a nitrate salt with an acid catalyst, applying this solution to a fabric, drying the fabric in a dryer by selecting the temperature in such a way that the bleaching reaction does not take place in a significant way during the drying step (e.g. less than 60 °C) and applying a laser beam to the fabric to generate nitrogen oxide compounds which attack the indigo dye and thereby create a color value change.

[0038] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by mixing a nitrate salt with an acid catalyst, applying this solution to a fabric, drying the fabric in a dryer by selecting the temperature in such a way that the bleaching reaction does not take place in a significant way during the drying step (e.g. less than 60 °C) and applying a laser beam in several passages (same or different pattern) to the fabric to generate nitrogen oxide compounds, which attack the indigo dye and thereby create a color value change.

[0039] One embodiment of the invention the material after application of nitrate is then stored for a certain period of time in order to obtain laser ready material and/or easy laser material and/or storable laser sensitive material. Fibers may be spun into yarns or combined to non-woven fabric, yarns may be woven or knitted into fabric and fabric may be cut and sewn into garments. All materials may be treated with methods used in the textile industry (e.g. ozone treatment, etc.) in continuous or batch processes in such a way that the nitrate compound is not washed away from the material. At a given time a laser beam is applied to the previously treated material in a single passage or in several passages (same or different pattern) to the fabric to generate nitrogen oxide compounds which attack the indigo dye and thereby create a color value change.

[0040] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by applying a solution comprising 20 – 35 vol% nitrate salt, optionally about 0.1 – 2 vol% of a different nitrate salt, and about 5.0 – 35.0 vol% acid catalyst, to a fabric, drying the fabric in a dryer at temperatures less than 60 °C, applying a laser beam to the denim to generate nitrogen oxide compounds which attack the indigo dye and thereby create a color value change.

[0041] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by applying a solution comprising 20 – 30 vol% $\text{Mg}(\text{NO}_3)_2$, optionally about 0.01 – 2 vol% of another nitrate salt and about 1.0 – 20.0 vol% tartaric acid to a fabric, drying the fabric in a dryer or oven at temperatures less than 60 °C, and then applying a laser beam to generate nitrogen oxide compounds, which attack the indigo dye and thereby create a color value change.

[0042] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by using a solution comprising about 5 – 20 vol% $\text{Al}(\text{NO}_3)_3$, optionally about 5 vol% butyl diglycol, mixing it with a solution of about 10 – 35 vol% toluenesulfonic acid and applying it to the fabric, drying the fabric in a dryer at temperatures less than 60 °C, applying a laser beam to the fabric to generate nitrogen oxide compounds, which attack the indigo dye and thereby create a color value change.

[0043] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by using a solution comprising about 10 vol% $\text{Al}(\text{NO}_3)_3$, optionally about 5 vol% butyl diglycol, mixing it with a solution of about 30 vol% toluenesulfonic acid and applying it to the fabric, drying the fabric in a dryer at temperatures less than 60 °C, applying a laser beam to the fabric to generate nitrogen oxide compounds which attack the indigo dye and thereby create a color value change.

[0044] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by applying a solution comprising about 0.1 – 20 vol% $\text{Al}(\text{NO}_3)_3$, optionally about 5 vol% butyl diglycol, and about 0.01 – 35 vol% toluenesulfonic acid to the fabric depending on the intensity of the desired effect, and drying the fabric (e.g. dryer, oven, fan, air dry, etc.) by selecting the temperature in such a way that the bleaching reaction does not take place in a significant way during the drying step (e.g. less than 60 °C), applying a laser beam to the fabric to generate nitrogen oxide compounds, which attack the indigo dye and thereby create a color value change.

[0045] A further embodiment of the invention relates to a method to increase the color value of laser treated fabric by applying a solution comprising about 0.1 – 20 vol% $\text{Al}(\text{NO}_3)_3$, optionally about 5 vol% butyl diglycol, and about 30 vol% toluenesulfonic acid to the fabric depending on the intensity of the desired effect, and drying the fabric (e.g. dryer, oven, fan, air dry, etc.) by selecting the temperature in such a way that the bleaching reaction does not take place in a significant way during the drying step (e.g.

less than 60 °C), applying a laser beam to the fabric to generate nitrogen oxide compounds, which attack the indigo dye and thereby create a color value change.

[0046] One embodiment of the invention relates to a method to increase the color value of laser treated fabric by applying a solution comprising an aluminum based nitrate salt, optionally a wetting agent, and toluenesulfonic acid to the fabric, drying the fabric, applying a laser beam to the fabric to generate nitrogen oxide compounds, which attack the indigo dye and thereby create a color value change.

[0047] One embodiment of the invention relates to a method to increase the color intensity of laser treated fabric by mixing a magnesium based nitrate salt with buffer compound containing a phosphoric acid and the corresponding salt of this acid, and applying this solution to fabric, and drying the fabric in a dryer at temperatures less than 60 °C, and applying a laser beam to the fabric to change the color intensity to value ranges of L from 15-40 to 30-60.

[0048] One embodiment of the invention relates to a method to increase the color intensity of laser treated fabric by mixing a magnesium based nitrate salt with catalyst, and applying this solution to fabric, and drying the fabric in a dryer at temperatures less than 60 °C, and applying a laser beam to the fabric to change the color intensity to value ranges of L from 15-30 to 30-60.

[0049] One embodiment of the invention relates to a method to increase the color intensity of laser treated fabric by mixing a magnesium based nitrate salt with catalyst, and applying this solution to fabric, and drying the fabric (e.g. dryer, oven, fan, air dry, etc.) by selecting the temperature in such a way that the bleaching reaction does not take place in a significant way during the drying step (e.g. less than 60 °C), and applying a laser beam to the fabric to change the color intensity to value ranges of L from 15-30 to 30-60.

[0050] One embodiment of the invention relates to the use of an aqueous solution applied to fabric to increase the color value of laser treated fabric.

[0051] One embodiment of the invention relates to the use of an aqueous solution containing magnesium salt and at least one of a buffer or a catalyst, and applying the aqueous solution to fabric to increase the color value of laser treated fabric.

[0052] One embodiment of the invention relates to a method to achieve Lab color space value ranges for L from 15 to 100.

[0053] One embodiment of the invention relates to a method to achieve Lab color space lightness value ranges for L of from 20 to 60 by laser treating fabric that has been pretreated with magnesium salt mixed with either a buffer or catalyst.

[0054] One embodiment of the invention relates to a method to increase the Lab color space lightness value L by 2 points by laser treating the fabric that has been pretreated with magnesium salt mixed with either a buffer or catalyst compared to the untreated fabric.

[0055] One embodiment of the invention relates to a method to increase the Lab color space lightness value L by 2 points by laser treating the fabric that has been pretreated with nitrate salt mixed with either a buffer or catalyst compared to the untreated fabric.

[0056] One embodiment of the invention relates to a method as described above wherein the drying step b) results in a color change that is lower than a lightness value of the fabric by 2 points.

[0057] One embodiment of the invention relates to an article obtained by a method as described above.

[0058] A further embodiment of the invention relates to the method as described above, wherein the applied compounds are non-hazardous.

[0059] A further embodiment of the invention relates to the method as described above, including the use of a thickening agent to increase the viscosity of the solution by at least 10%.

[0060] A further embodiment of the invention relates to the method as described above, wherein the thickening agent is a polymer.

[0061] A further embodiment of the invention relates to the method as described above, wherein the drying temperature is kept below a critical temperature which would cause the reaction to proceed with a noticeable color value effect.

[0062] A further embodiment of the invention relates to the method as described above, wherein the ratio of the buffer to the magnesium salt ranges from 3:1 to 1:10.

[0063] A further embodiment of the invention relates to the method as described above, wherein the concentration of the catalyst ranges from 0.1% to 10%.

[0064] A further embodiment of the invention relates to the method as described above, including the use of a wetting agent in a concentration of 0.1-5% to increase the penetration of the solution.

[0065] A further embodiment of the invention relates to the method as described above, including the use of a softening agent in a concentration of 0.1-20% to increase the penetration of the solution.

[0066] A further embodiment of the invention relates to the method as described above, wherein the softening agent is a polymer.

[0067] A further embodiment of the invention relates to the method as described above, wherein the softening agent is a glycol derivative.

[0068] A further embodiment of the invention relates to the method as described above, wherein one auxiliary agent is a plastic compound (e.g. PMMA, PVC, PE, PP, each in modified and unmodified form, etc.).

[0069] A further embodiment of the invention relates to the method as described above, wherein one auxiliary agent is a silica/silicate compound (e.g. amorphous or crystalline SiO_2 , sodium silicate etc.).

[0070] A further embodiment of the invention relates to the method as described above, wherein the aqueous solution comprises about 25 vol% of a nitrate salt, a of phosphate buffer from about 1.0 to 10 vol% and optionally any auxiliary agent ranging from 0.01 to 20 vol%.

[0071] The above said auxiliary agent is selected from the group consisting of another nitrate, a softener, brightening agent, plastic, natural and synthetic polymers, SiO_2 , silicates, a thickening agent, dyestuff used as a marker dye, a wetting agent, a complexing agent, a dispersing agent, and a buffer solution derived from the salt of an acid and the corresponding acid.

[0072] A further embodiment of the invention relates to the method as described above, wherein the solution comprises an organic (nitro-)compound, which is releasing NO_x after laser activation and/or other heat activation.

[0073] A further embodiment of the invention relates to the method as described above, wherein the solution comprises a compound, which increases the laser energy uptake of the treated material.

[0074] A further embodiment of the invention relates to the method as described above, wherein the solution comprises a compound, which changes the laser light scattering/adsorbing/emitting behavior on the surface of the material.

[0075] A further embodiment of the invention relates to the method as described above, wherein the solution comprises a compound, which gets cleaved/activated in a

first step by a laser treatment and the resulting products are eventually inducing the actual nitrate bleaching mechanism.

[0076] A further embodiment of the invention relates to the method as described above, wherein the aqueous solution comprises about 25 vol% of a nitrate salt, of about 1.0 to 10 vol% $KAl(SO_4)_2$ and optionally any auxiliary agent ranging from 0.01 to 20 vol% where the agent can be selected from the group nitrates, polymers, marker dyes, complexing agents, wetting agents, softening agents and dispersing agents.

[0077] One embodiment of the invention relates to a fabric obtained by a method as described above.

Description of embodiments

[0078] The invention discloses a novel combination of a non hazardous chemical treatment to denim followed by a laser treatment which together provide the abrasion intensity to simulate the worn out look on denim jeans without the use of the dangerous potassium permanganate chemical. Surprisingly, other unexpected benefits were realized from this invention in terms of increased laser throughput and/or reduced laser power requirements.

[0079] Now there are a number of chemicals that could oxidize indigo to produce a bleached effect such as enzymes, hypochlorite, organo peroxides, zinc nitrate and potassium permanganate. However, these chemicals are hazardous and thus do not solve the industry problem. Further, the authentic worn look is generated by fading effects which cannot be achieved when these products are sprayed or brushed, or when the garments are immersed. The application of the chemicals on denim do not allow for the creation of the authentic worn out looks because they do not achieve the abraded pattern change in an intensity to satisfactorily simulate the feathering characteristics of worn out jeans.

[0080] It is also known in the prior art that the magnesium salt $Mg(NO_3)_2$ can generate compounds that oxidize the indigo dye in denim and produce bleached effects. The respective relevant chemical reaction is:



[0081] The chemical reaction generates nitrogen oxides which attack or oxidize the Indigo dye at the denim. The NO_2 can be a variety of nitrogen oxide (NO_x) compounds, such as N_2O , N_2O_3 , NO_2 , N_2O_4 , NO_3 , N_2O_4 , N_2O_5 , NO_3 , N_2O_6 and NO . NO_x is

hazardous by itself but it is either consumed by the indigo or evaporated and immediately exhausted with the laser fumes, so it is not hazardous to the workers. However, to promote the chemical reaction so as to achieve noticeable bleaching effects on denim, the magnesium salt is applied to denim and then the treated denim is heated at temperatures of about 140 °C for about 20 minutes. The activation energy to promote the chemical reaction is dependent upon both time and temperature. So applying a laser process to the denim treated with the magnesium salt will not generate the chemical reaction and thus will not produce a bleached effect even though the laser temperature is much higher than 140 °C.

[0082] Laser systems are used in fashion design, pleating, cutting and modification of fabric surface to impart some special finish. Laser fading works with better precision and higher productivity but also have some drawbacks. The laser works by creating extensive heat. Within the focused region, the material is subject to very intensive heating within a very small region and time. Laser energy is absorbed as heat and the material rapidly heats leading to melting as a phase change from solid to liquid takes place.

[0083] Irradiation may be applied by a laser device that emits light through a process of optical amplification based on the stimulated emission of electromagnetic radiation.

[0084] Most lasers, for example Nd:YAG lasers, many fiber lasers and the most powerful laser diodes emit near-infrared light. There are comparatively few laser sources for the mid- and far-infrared spectral regions. CO₂ lasers can emit at 10.6 μm and some other wavelengths in that region.

[0085] The technology of lasers for the generation of ultraviolet light faces various challenges; nevertheless, there are a few kinds of ultraviolet lasers which can directly generate UV light: some bulk lasers (e.g. based on cerium-doped crystals such as Ce:LiCAF), fiber lasers, laser diodes (mostly GaN-based), dye lasers, excimer lasers, and free electron lasers.

[0086] According to one embodiment of the invention the pretreated textile material is placed under a laser device and then scanning a laser beam having a selected wavelength, power density, pulse width, and repetition rate over the textile material until the desired degree of fading and/or worn appearance or the selected pattern is achieved.

[0087] The laser may be a q-switched Nd:YAG laser with a wavelength of about 1064 nanometers, although other lasers, such as CO₂ gas lasers or excimer gas lasers may be utilized. The wavelength of the laser is chosen to give optimal dye photo-decomposition without affecting the textile material.

[0088] The scanning of the laser beam over the textile material may be controlled by galvanometric mirror, acousto-optic deflector, deflector, magneto-optic beam deflector, polygon mirror, or a moving holographic optical element.

[0089] Other possible wavelengths for other laser sources range between 190 nanometers to 10600 nanometers. An excimer laser may operate effectively at wavelengths of 196 nm to 235 nm, or a CO₂ laser may operate effectively at 10600 nanometers. The wavelength of the laser should be chosen such that it is strongly absorbed by the dye to be faded but not by the textile material. The range of pulse duration used has been from 5 nanoseconds to 100 microseconds, with the best results being from 20 to 350 nanoseconds. Other variables, such as the pulse energy, peak power, scan speed, dot pitch, and energy density play an important factor in the degree of photo-decomposition and the avoidance of damage to the textile material.

[0090] For example, these variable parameters may include the laser beam having a repetition rate from 1 hertz to 500 MHz (500×10^6 hertz), a pulse duration between approximately 10 fs (10×10^{-15} seconds) to 500 ms (500×10^{-3} seconds), the laser beam may have a continuous output beam and is classified as a cw laser, a pulsed laser, or the laser beam have a scan speed of 1 mm per minute to 500 meter/second, and a dot pitch between 0.1 μ m to 5 meters.

[0091] Through the pretreatment of the textile material with a nitrate compound an improved fading is achieved. In addition, the textile material is less damaged, e.g. prevents burned surface of the fibers or less damage to synthetic fibers. Further advantages of the present invention are a working environment in a continuous process, faster cycle times and fewer cycles conducted over the textile material, or less laser power needed, which again leads to less damages of the textile material and better chemical uptake (e.g. dyeability) of the laser treated areas.

[0092] Numerous chemical compound combinations were trialed with laser treatment, examples of which are shown in Tables 1-7.

[0093] One embodiment of the invention relies upon the non hazardous magnesium salt chemical and its reaction to generate the NO_x compounds, but in addition, mixing

the salt with a buffer to both lower the activation temperature and to control the pH value at a non-hazardous level. For example, one preferred buffer is H_3PO_4 + NaH_2PO_4 . Potassium could replace sodium and of course other buffer compounds that accomplish an increase in pH level can be used.

[0094] Another embodiment of the invention is to use a two component solution consisting of the acid and its corresponding salt.

[0095] Another embodiment is to use an aqueous solution of a nitrate salt and buffer.

[0096] Another embodiment of this invention relies upon the magnesium salt chemical reaction to generate the NO_x compounds, but in addition, mixing the salt with a catalyst to decrease the reaction temperature and to control the pH value.

[0097] Another embodiment of this invention is to achieve a non hazardous solution according to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) and non hazardous classification according to REACH SVHC list, the Restricted Substance Lists of various Labels like Levi Strauss & Co, and GOTS, the Global Organic Textile Standard. If the material gets a hazardous sign in the MSDS, it is classified as hazardous. If the material is listed in the RSL list it is not allowed in the manufacturing plant because it is deemed hazardous. In the present invention the term "textile material" or "fabric" are used interchangeably and refer to fibers, yarns, fabrics, flexible knitted, woven or non-woven material consisting of a network of natural or artificial fibers (yarn or thread). The textile material may be used in production of further goods (cloths, garments, carpets, bags, shoes, jewelry, furnishings, artifacts, etc.).

[0098] In one embodiment of the invention the textile material is finished colored denim. In one further embodiment of the invention the method may be applied to a variety of garments including jeans, jean jackets, jean skirts, jean shorts, jean dresses, jean vests, corduroy and twill garments. The method may also be applied on other fabrics besides denim fabrics.

[0099] The textile material may be dyed or coated with a dye, preferably with a natural or synthesized dye. In one embodiment of the invention the fabrics are dyed with an indigo dye, which may be a natural or synthesized indigo dye, or sulphur black dye. In another embodiment of the invention the yarns of the fabrics are dyed with sulphur black dyes, a combination of indigo dye and sulphur black dye or a combination of sulphur black below, in-between and on top of the indigo dye on the yarn.

[00100] The textile material may consist of cellulosic material (e.g. natural fibers like bast fibers (e.g. jute, flax, hemp, etc.), leaf fibers (e.g. sisal, etc.), seed fibers (e.g. cotton, etc.), or other fibers like bamboo, etc., or man-made fibers like lyocell type, viscose and rayon type, or modal type, cupro type, acetate type), and in special cases also fibers based on proteins (e.g. soja, casein, fibroin, sericin, etc.), starch and glucose (e.g. polylactide fibers, etc.), alginates and chitosanes, but not limited to, and may be used in a combination of synthetic fiber types derived from polycondensation (e.g. polyester, polyethyleneterephthalate, polyamide, polyimide, polyamide-imid, polyphenylsulfide, aramide, etc.), polymerization (e.g. polyacrylonitrile, polytetrafluorethylene, polyethylene, polypropylene, polyvinylchloride, etc.) and fibers produced by polyaddition procedure (e.g. polyurethane, etc.), but not limited to.

[00101] The nitrogen compound may be an organic nitro- or nitrate-compound like an aliphatic, aromatic, heterocyclic or a biochemical organic compound selected from the group consisting of alkanes, alkenes, alkynes, cyclic compounds, as well as allyl-, alkyl-, arylcompounds, alcohols, aldehydes, esters, ethers, ketones, carbohydrates, or inorganic nitrates of heavy metals or of an alkali-metal, alkaline earth metal, or one of the boron group, carbon group, nitrogen group, chalcogens, halogens, noble gases, as well as from the group of transition metals, Lanthanides and Actinides.

[00102] In one embodiment of the invention the nitrogen compound is a nitrate salt which is selected from the group consisting of $\text{Mg}(\text{NO}_3)_2$, KNO_3 , LiNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, NaNO_3 , RbNO_3 , CsNO_3 , $\text{Be}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sc}(\text{NO}_3)_3$, $\text{Ti}(\text{NO}_3)_4$, $\text{Zr}(\text{NO}_3)_4$, $\text{VO}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$, AgNO_3 , $\text{Cd}(\text{NO}_3)_2$, $\text{Hg}_2(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $[\text{B}(\text{NO}_3)_4]^-$, $\text{Ga}(\text{NO}_3)_3$, $\text{Ti}(\text{NO}_3)_3$, $\text{Pb}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, FNO_3 , ClNO_3 , $\text{Xe}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_4$, $\text{UO}_2(\text{NO}_3)_2$, $\text{Gd}(\text{NO}_3)_3$, as well as their salts with nitrite.

[00103] In one embodiment of the invention the nitrate salt is selected from the group consisting of $\text{Mg}(\text{NO}_3)_2$, LiNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{Zn}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_4$, as well as their respective salts with nitrite.

[00104] The nitrate salt may be used in a concentration of higher than 0.5 g/L, limited by its solubility in the solvent. In one embodiment a mixture of nitrate salts is used. In one further embodiment the nitrate salt or mixture is used in a dry form, e.g. as a powder.

[00105] Appropriate solvents are polar and/or low-polarity solvents as primary solvents or as mixtures or emulsions in any desired ratio, such as water, alcohols, fatty alcohols, aliphatic fatty alcohols, aromatic fatty alcohols, amines, octylamines, cyclic amines, hydrocarbon solvents, naphthenic solvents, paraffinic solvents, aromatic derivatives such as diisopropylnaphthalene, glycols, polyglycols, esters, branched monoesters, oleic esters, benzoic esters, lactic acid esters, myristic acid esters, palmitic acid esters, fatty acid esters in general, propylene glycol acetates, dipropylene glycol ether acetate, polyethylene glycol acetates, diethylene glycol monobutyl ether acetate, glycol ethers, polypropylene glycol esters, tripropylene glycol monomethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, propylene glycol phenyl ether, tripropylene glycol monobutyl ether and polyethylene glycol ethers, hexyl carbitol ether, phenols, alkylphenols, fatty acids, terpene alcohols, terpene oils, copolymers of vinylpyrrolidone, polyglycols and polypropylene glycol. The solvent may further include additives such as dispersants, wetting agents, anti-foaming agents, softeners, plastics, thickeners, etc.

[00106] The acid may be an Arrhenius acid, Brønsted-Lowry acid or a Lewis acid, chemically characterized as monoprotic or polyprotic acids or salts thereof which may be mineral acids (inorganic acids) or organic acids like sulfonic acids or salts thereof, aliphatic or aromatic carboxylic acids, amino acids, halogenated carboxylic acids and vinylogous carboxylic acid or salts thereof. In one embodiment of the invention the acid may be selected from the group consisting of sulfuric acid, hydrochloric acid, fluorosulfuric acid, phosphoric acid, fluoroantimonic acid, fluoroboric acid, hexafluorophosphoric acid, chromic acid, boric acid, methanesulfonic acid, ethanesulfonic acid, amidosulfonic acid, sulfamidic acid, sulfanilic acid, benzenesulfonic acid, toluenesulfonic acids, trifluoromethanesulfonic acid, polystyrene sulfonic acid, acetic acid, citric acid, formic acid, gluconic acid, glycolic acid, lactic acid, tartaric acid, oxalic acid, maleic acid, pyruvic acid, benzoic acid, gallic acid, barbituric acid, dihydroxybenzoic acid, cinnamic acids, aminobutyric acid, fumaric acid, malic acid, succinic acid, malonic acid, glutaminic acid, nitrosalicylic acid, nitrobenzoic acids, nitrobenzenesulfonic acid, levolinic acid, pimelic acid, salicylic acid, sulfosalicylic acid, adipic acid, caprylic acid, nicotinic acids, uric acid, phthalic acid, chloroacetic acid, fluoroacetic acid, trifluoroacetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, ascorbic acid, aspartic acid, and mandelic acid. Mixtures of two or

more of these compounds may also be used, as well as in a combination with corresponding salts to form buffer solutions.

[00107] The acid catalyst may be for example selected from the group consisting of organic or inorganic compounds, i.e. organic or inorganic forms of chlorides, sulfates, phosphates, borates, fluorides, Lewis acid chlorides, such as ferric chloride, zinc chloride and aluminum chloride, magnesium chloride, ammonium chloride, potassium aluminum sulfate, ammonium sulfate, maleate ester, an amino acid hydrochloride, such as glycine hydrochloride, glutamic acid hydrochloride, betaine hydrochloride, alanine hydrochloride, valine hydrochloride, lysine hydrochloride, arginine hydrochloride, or aspartic acid hydrochloride.

[00108] Suitable acid catalysts include organic acids such as citric acid and tartaric acid. Magnesium chloride, ammonium chloride, zinc chloride, zinc fluoroborate and zinc nitrate are suitable (weak) acids, as well as water soluble salts of mono-, di-, tri- and polyphosphates (e.g. monosodium phosphate, disodium phosphate, trisodium phosphate, monopotassium phosphate, dipotassium phosphate, tripotassium phosphate, monomagnesium phosphate, dimagnesium phosphate, trimagnesium phosphate, ammonium polyphosphate, monoammonium phosphate, diammonium phosphate, triammonium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, disodium pyrophosphate, trisodium pyrophosphate, tetrasodium pyrophosphate, sodium triphosphate, pentapotassium triphosphate), and pyrophosphates or organophosphates which are esters of phosphoric acid and phytinic acid and their corresponding salts; as well as complexing agents which may be but not limited to selected from the list of methylglycindiacyetic acid, ethylenediaminetetraacetic acid, L-glutamic acid *N,N*-diacyetic acid tetra sodium salt, alanine-*N,N*-diacyetic acid trisodium salt, diethylene triamine pentaacetic acid, nitrilotriacetic acid, ethylene glycol tetraacetic acid, ethylenediamine-*N,N'*-disuccinic acid, polycarboxylates, zeolithes, and phosphonates. Mixtures of two or more of these compounds may also be used, as well as in combination to form buffer solutions.

[00109] Preferred solute concentrations of the acid depend upon the particular acid catalysts used. Lower concentrations of highly active compounds may be used to avoid unwanted acid damage to the fabric and higher concentrations of less active compounds.

[00110] The solution of the acid together with the nitrate is preferably an aqueous solution, but it may be also applied in separate steps or in a mixture of the pure substances in powder form. One or more components may be encapsulated in the solution or the solid form. The textile material may be evenly or unevenly impregnated with this composition using any of the conventional techniques.

[00111] The application of one or more components together or in separate form on the fibers, yarns, fabrics or garments may be performed by immersion, padding, spraying, brushing, printing, foaming, sponging, other contact methods like stone and/or powder carrier, but not limited to, at any stage of processing. In one embodiment of the invention the aqueous solution is sprayed on the raw or desized denim garment on limited areas, or covering all parts of the garment, to create localized bleached effects simulating wear areas on the jeans or applied on prepared shaped motif to jeans or fabric which can be subsequently washed to highlight the applied areas. In another embodiment of the invention the solution may be applied on fabric form by immersion or as a one side application by printing (e.g. as block printing or roller cage printing), spraying, foaming, or a kiss roll on all areas of the application side or on limited areas of the application side.

[00112] The acid catalyst may be applied in a concentration of higher than 0.01 g/L, limited by its solubility in the solvent. In one embodiment a mixture of acids may be used.

[00113] In one embodiment of the invention the ratio of acid catalyst to the nitrate salt in the reaction mixture is in the range of about 75:1 to 1:100, preferably in the range of about 20:1 to 1:20, more preferably in the range of 5:1 to 1:20, most preferred in the range of 1:1 to 1:5.

[00114] Additionally one or more further catalysts may be added to the reaction mixture such as for example a sulfate compound, phosphate compound, ammonium compound and/or a chloride compound, or mixtures thereof.

[00115] In one embodiment of the invention addition of a buffer solution might be appropriate. Suitable buffer solutions are well known to a person skilled in the art.

[00116] In one embodiment of the invention the method is carried out in the presence of a sulfate, a phosphate and/or chloride catalyst. The sulfate may be selected from the group consisting of MgSO_4 , $\text{Ce}(\text{SO}_4)_2$, VOSO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CuSO_4 , $\text{KAl}(\text{SO}_4)_2$, $\text{Al}_2(\text{SO}_4)_3$, ZnSO_4 , NaHSO_4 , KHSO_4 , Li_2SO_4 , CaSO_4 . The phosphate may

be selected from the group of calcium, sodium, potassium and ammonium phosphates such as NaH_2PO_4 , Na_2HPO_4 , KH_2PO_4 , K_2HPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaHPO_4 , $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_3\text{HP}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{K}_5\text{P}_3\text{O}_{10}$, $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$. The chloride may be selected from heavy metal chloride such as for example from ZnCl_2 , FeCl_3 , FeCl_2 , CuCl_2 , MnCl_2 , CoCl_2 , NiCl_2 or AlCl_3 .

[00117] In one embodiment of the invention the textile material is treated with $\text{Mg}(\text{NO}_3)_2$ in the presence of methanesulfonic acid for about 30 min.

[00118] In one embodiment of the invention the textile material is treated with $\text{Mg}(\text{NO}_3)_2$ in the presence of tartaric acid and optionally another nitrogen compound for about 20 min at a temperature of about 60 °C.

[00119] In one embodiment of the invention the textile material is treated with an aqueous solution comprising at least one nitrate salt – depending on the cation species – in a concentration of about 1 – 80 vol%, or of about 5 – 75 vol%. In one embodiment of the invention the aqueous solution comprises at least one nitrate compound in a concentration of about 1 vol%, 2.5 vol%, 5 vol%, 7.5 vol%, 10 vol%, 15 vol%, 18 vol%, 20 vol%, 25 vol%, 26.6 vol%, 28 vol%, 30 vol%, 32.5 vol%, 35 vol%, 38.5 vol%, 40 vol%, 42.5 vol%, 45 vol%, 47.5 vol%, 50 vol%, 51 vol%, 52 vol%, 55 vol%, 57 vol%, 60 vol%, 62.5 vol%, 65 vol%, 67.5 vol%, 70 vol%, 72.5 vol%, or 75 vol%.

[00120] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt in a concentration as stated above, wherein said nitrate salt is selected from the group consisting of $\text{Mg}(\text{NO}_3)_2$, LiNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, KNO_3 , NaNO_3 , $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\text{Co}(\text{NO}_3)_2$, or $\text{Fe}(\text{NO}_3)_2$, or hydrates thereof. Optionally, the aqueous solution may also comprise auxiliary agents.

[00121] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt in a concentration as stated above and at least one acid catalyst in a concentration of about 0.01 vol%, 0.05 vol%, 1.0 vol%, 1.25 vol%, 1.5 vol%, 1.75 vol%, 2.0 vol%, 2.25 vol%, 2.5 vol%, 2.75 vol%, 3.0 vol%, 3.25 vol%, 3.5 vol%, 3.75 vol%, 4.0 vol%, 4.25 vol%, 4.5 vol%, 4.75 vol%, 5.0 vol%, 5.25 vol%, 5.5 vol%, 5.75 vol%, 6.0 vol%, 6.25 vol%, 6.5 vol%, 6.75 vol%, 7.0 vol%, 7.25 vol%, 7.5 vol%, 7.75 vol%, 8.0 vol%, 8.25 vol%, 8.5 vol%, 8.75 vol%, 9.0 vol%, 9.25 vol%, 9.5 vol%, 9.75 vol%, 10.0 vol%, 11.0 vol%, 12.0 vol%, 13.0 vol%, 14.0 vol%, 15.0 vol%, 17.5 vol%, 20.0 vol%, 22.5 vol%, or 25.0 vol%.

[00122] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt and at least one acid catalyst in a concentration as stated above, wherein said acid catalyst is selected from the group consisting of MgSO_4 , $\text{Ce}(\text{SO}_4)_2$, VOSO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnCl_2 , FeCl_3 , CuCl_2 , FeCl_2 , AlCl_3 , LiNO_3 , CaCl_2 , NaCl , KCl , LiCl , SrCl_2 , MgCl_2 , $(\text{NH}_4)_2\text{SO}_4$, CuSO_4 , Li_2SO_4 , $\text{NH}_4\text{Al}(\text{SO}_4)_2$, $\text{KAl}(\text{SO}_4)_2$, ZnSO_4 , NaH_2PO_4 , Na_2HPO_4 , KH_2PO_4 , K_2HPO_4 , $\text{Zn}_3(\text{PO}_4)_2$, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaHPO_4 , $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_3\text{HP}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{K}_5\text{P}_3\text{O}_{10}$, $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ or hydrates thereof.

Optionally, the aqueous solution may also comprise auxiliary agents.

[00123] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt in a concentration as stated above and at least one acid catalyst in a concentration of about 0.01 vol%, 0.05 vol%, 1.0 vol%, 1.25 vol%, 1.5 vol%, 1.75 vol%, 2.0 vol%, 2.25 vol%, 2.5 vol%, 2.75 vol%, 3.0 vol%, 3.25 vol%, 3.5 vol%, 3.75 vol%, 4.0 vol%, 4.25 vol%, 4.5 vol%, 4.75 vol%, 5.0 vol%, 5.25 vol%, 5.5 vol%, 5.75 vol%, 6.0 vol%, 6.25 vol%, 6.5 vol%, 6.75 vol%, 7.0 vol%, 7.25 vol%, 7.5 vol%, 7.75 vol%, 8.0 vol%, 8.25 vol%, 8.5 vol%, 8.75 vol%, 9.0 vol%, 9.25 vol%, 9.5 vol%, 9.75 vol%, 10.0 vol%, 11.0 vol%, 12.0 vol%, 13.0 vol%, 14.0 vol%, 15.0 vol%, 16.0 vol%, 17.0 vol%, 18.0 vol%, 19.0 vol%, 20.0 vol%, 22.5 vol%, 25.0 vol%, 27.5 vol%, 30.0 vol%, 32.5 vol%, 35.0 vol%, 37.5 vol%, 40.0 vol%, 42.5 vol%, 45.0 vol%, 47.5 vol%, or 50.0 vol%.

[00124] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt in a concentration as stated above and at least one acid catalyst, wherein said acid catalyst is selected from the group consisting of methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$), phosphoric acid, citric acid, tartaric acid, oxalic acid, HCl , maleic acid, H_2SO_4 , lactic acid, succinic acid or malonic acid. Optionally, the aqueous solution may also comprise auxiliary agents.

[00125] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt, at least one acid in respective concentrations as stated above and optionally auxiliary agents.

[00126] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt, optionally at least one acid catalyst in respective concentrations as stated above and a thickening agent in a concentration of about 0.01 – 1 vol%, of about 0.05 – 0.75 vol%, or of about 0.1 – 0.5 vol%. Preferably, the thickening agent is modified starch, modified cellulose, alginate or xanthan gum, but also hyaluronic acid,

gelatine (collagen), pectin, agar (agarose), guar gum, gum arabic, carrageenan, locust bean gum (galactomannan), tragacanth and gellan gum.

[00127] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt, optionally at least one acid catalyst, and additionally auxiliary chemical agents in a concentration of about 0.001 – 25 vol%, of about 0.01 – 7.7 vol%, or of about 0.025 – 5.0 vol%. Preferably, the auxiliary component in respective concentrations as stated above is selected from the group consisting of a nitrate, softener, brightening agent, plastic, a thickening agent, dyestuff used as a marker dye, a wetting agent, a complexing agent, a dispersing agent, and buffer components being derived from the salt of an acid and/or the corresponding acid.

[00128] In a further embodiment of the invention the aqueous solution comprises at least one nitrate salt, optionally at least one acid and optionally a thickening agent in respective concentrations as stated above and additionally auxiliary chemicals in a concentration of about 0.001 – 10 vol%, of about 0.05 – 7.7 vol%, or of about 0.1 – 5.0 vol%. Preferably, the auxiliary component is selected from the group consisting of a polysorbate, alkyl polyglycoside, methyl red, chromene red, monosodium phosphate, disodium pyrophosphate, tetrasodium diphosphate, butyl diglycol, sodium dodecyl sulfate, sodium olefin sulfonate, sodium laureth sulfate, sodium lauryl ether sulfate, alanine-*N,N*-diacetic acid trisodium salt, glutamine-*N,N*-diacetic acid trisodium salt, DMSO and sulfolane. Respective softeners are fatty alcohol polyglycol ether, acrylic acid, 3,5,7-trimethyldecane, soap, triglycerides, polydimethylsiloxane, cyclopentasiloxan, emulsifiers, lignosulfonate, cationic surfactants, anionic surfactants, esterquats, ionic liquids, sodium 2-ethylhexyl sulfate, 2-methyl-2,4-pentanediol, tributyl phosphate, triisobutyl phosphate, 1-hydroxyethane-1,1,-diphosphonic acid (HEDP), 2,2-dimethyl-1,3-propanediol. Oxidizers as respective additives could be peroxides, peroxy acids and/or persulfates.

[00129] In a further embodiment of the invention the aqueous solution comprises $\text{Mg}(\text{NO}_3)_2$, another nitrate compound and optionally a complexing agent. Tartaric acid is added to create the used/vintage look.

[00130] In a further embodiment of the invention the aqueous solution comprises about 26 vol% $\text{Mg}(\text{NO}_3)_2$, about 0.05 – 0.1 vol% of another nitrate compound and added to create the used/vintage look. The composition may further include about 0.01 – 15 vol% of at least one auxiliary agent selected from the group consisting of a nitrate,

a thickening agent, dyestuff used as a marker dye, a wetting agent, a complexing agent, a dispersing agent, and a buffer solution being derived from the salt of an acid and the corresponding acid.

[00131] A further embodiment of the invention relates to the use of an aqueous composition comprising at least one nitrate salt and optionally at least one acid and/or auxiliary agent for the treatment of textile material in order to obtain a used and/or vintage look.

[00132] A further embodiment of the invention relates to the use of an aqueous composition comprising at least one nitrate salt and at least one acid catalyst for the treatment of textile material in order to obtain a used and/or vintage look, wherein the acid catalyst is selected from the group consisting of MgSO_4 , $\text{Ce}(\text{SO}_4)_2$, VOSO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnCl_2 , FeCl_3 , CuCl_2 , FeCl_2 , AlCl_3 , LiNO_3 , CaCl_2 , NaCl , KCl , LiCl , SrCl_2 , MgCl_2 , $(\text{NH}_4)_2\text{SO}_4$, CuSO_4 , Li_2SO_4 , $\text{NH}_4\text{Al}(\text{SO}_4)_2$, $\text{KAl}(\text{SO}_4)_2$, $\text{Zn}_3(\text{PO}_4)_2$, NaH_2PO_4 , Na_2HPO_4 , KH_2PO_4 , K_2HPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaHPO_4 , $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_3\text{HP}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{K}_5\text{P}_3\text{O}_{10}$, $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, or hydrates thereof.

[00133] A further embodiment of the invention relates to the use of an aqueous composition comprising at least one nitrate salt and at least one acid catalyst for the treatment of textile material in order to obtain a used and/or vintage look, wherein the acid catalyst is selected from the group consisting of methanesulfonic acid, citric acid, tartaric acid, oxalic acid, HCl , maleic acid, H_2SO_4 , lactic acid, or malonic acid or mixtures thereof.

[00134] A further embodiment of the invention relates to the use of an aqueous composition comprising at least one nitrate salt and at least one acid catalyst for the treatment of textile material in order to obtain a used and/or vintage look, wherein the acid catalyst and/or acidic buffer component is selected from the group consisting of MgSO_4 , $\text{Ce}(\text{SO}_4)_2$, VOSO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnCl_2 , FeCl_3 , CuCl_2 , FeCl_2 , AlCl_3 , CaCl_2 , NaCl , KCl , LiCl , SrCl_2 , MgCl_2 , $(\text{NH}_4)_2\text{SO}_4$, CuSO_4 , Li_2SO_4 , $\text{NH}_4\text{Al}(\text{SO}_4)_2$, $\text{KAl}(\text{SO}_4)_2$, $\text{Zn}(\text{NO}_3)_2$, NaH_2PO_4 , Na_2HPO_4 , KH_2PO_4 , K_2HPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaHPO_4 , $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_3\text{HP}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{K}_5\text{P}_3\text{O}_{10}$, $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ or hydrates thereof, or wherein the acid catalyst is selected from the group consisting of methanesulfonic acid, toluenesulfonic acid, citric acid, tartaric acid, oxalic acid, HCl , maleic acid, H_2SO_4 , lactic acid, succinic acid or malonic acid, and optionally comprising at least one further auxiliary chemical and/or thickening agent.

[00135] A further embodiment of the invention relates to the use of an aqueous solution comprising about 26 vol% $\text{Mg}(\text{NO}_3)_2$, about 0.05 vol% of another nitrate, about 2.0 vol% tartaric acid and optionally about 0.01 vol% chelating agent for the treatment of textile material in order to obtain a used look, a vintage look or a change in the color, optionally on preselected areas of the textile material.

[00136] In a further embodiment the colour value changes and can be measured in a ΔL value of 2 between the untreated and treated part. L stands for the lightness in the CIE 1976 Lab color space. A color value means the lightness or darkness of the color of the desired effect which can also be referred to as color intensity or the degree of whiteness or degree of brightness.

[00137] In a further embodiment isatin, anthranilic acid (2-aminobenzoic acid) and carbamic acid are formed due to the general oxidation reaction of indigo by the combined nitrate and acid treatment. Other reaction products are 5-nitroisatin, 5-nitrosalicylic acid and picric acid, which are formed due to the specific oxidation of indigo by the action of nitrate compounds. These products may be analyzed e.g. by means of NMR, liquid chromatography or gas chromatography after appropriate sample preparation or derivatization, respectively, of the mentioned products.

[00138] In a further embodiment the anhydroglucose units of the denim material may be esterified on positions 2, 3 and/or 6 by action of the nitrate compound under given conditions.

[00139] According to the inventive process bleaching occurs after the pre-treatment of the fabric and subsequent laser abrasion.

[00140] Additionally further textile auxiliary chemicals may be added in any combination and concentration in solid or liquid form to improve the usability and performance of the product according to what is required: e.g. dispersants, wetting agents, surfactants, softener, thickening agents, plastics, colorants, tinting agents, silicones, levelling agents, antifoams, antimigration agents, antibackstaining agents, softeners, stabilizers and optical brightening agents. These additives are well known to experts in the field and can be chosen according to commonly used concentrations depending on the desired effect, e.g. 0.001 – 10 vol%. Colorants may be selected from but not limited to dispersing dyes, acid dyes, basic dyes, vat dyes, Sulphur dyes, azoic dyes like methylene red and others. Food dyes like Fast Green FCF, Erythrosine, Tartrazine, Sunset Yellow FCF, Citrus Red 2, Orange B, Quinoline Yellow, Carmoisine,

Ponceau 4R, Patent Blue V, Green S, Allurared AC, , Amaranth, Anthocyane, Azorubin, Betanin, Brown FK, Brown HT, Brilliant blue, Brilliant black, Canthaxanthin, Carotin, Annatto (Norbixin), Capsanthin, Lycopin, 8'-Apo- β -caroten-8'-al, Ethyl-8'-apo- β -caroten-8'-oat, Chinolin yellow, Chlorophyll, Cochenille red A, Curcumin, Iron oxide, Erythrosin, Yellow orange, Gold, Green S, Indigotin, Cochenille, Lactoflavin, Litholrubin BK, Lutein, Patent Blue V, Riboflavin, Silver, Tartrazin, Titanium dioxide, Zeaxanthin, as well as duramine (e.g. Red), chromene (e.g. Red, Blue, Yellow), Evron Red may also be used. Other auxiliaries or their ingredients may be selected from but not limited to Tween 20, butyl diglycol, sodium dodecyl sulfate, sodium olefin sulfonate, sodium laureth sulfate, sodium lauryl ether sulfate, alanine-*N,N*-diacetic acid trisodium salt, glutamine-*N,N*-diacetic acid trisodium salt, DMSO and sulfolane. Respective softeners are fatty alcohol polyglycol ether, acrylic acid, 3,5,7-trimethyldecane, soap, triglycerides, polydimethylsiloxane, cyclopentasiloxan, emulsifiers, lignosulfonate, cationic surfactants, anionic surfactants, esterquats, ionic liquids, sodium 2-ethylhexyl sulfate, 2-methyl-2,4-pentanediol, tributyl phosphate, triisobutyl phosphate, 1-hydroxyethane-1,1,-diphosphonic acid (HEDP), 2,2-dimethyl-1,3-propanediol. Oxidizers as respective additives could be peroxides, peroxy acids and/or persulfates. Thickening agents may be selected from but not limited to products which are commonly used in textile auxiliaries, food additives, cosmetics and personal hygiene products, i.e. starch and modified starches, cellulose and modified cellulose (i.e. methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, hydroxypropylmethyl cellulose, hydroxypropyl cellulose, ethylhydroxyethyl cellulose), alginates (i.e. sodium-, potassium-, ammonium-, propylenglycol alginate), gum arabic, carrageen, agar-agar, Ceratonia silique, guar gum, Traganth, gellan, pectin, gelatin. Other chemicals may be added to impart more desirable improvement of the substrate in hand feel or other properties like softness, waterproofing, anti-microbial or microbe reducing chemicals, encapsulated perfumes, etc., or co-solvents (alcohols, ketones, nonionic solvents, ionic solvents, ionic liquids, etc.).

Examples

[00141] The Examples which follow are set forth to aid in the understanding of the invention but are not intended to, and should not be construed to limit the scope of the invention in any way. The Examples do not include detailed descriptions of

conventional methods. Such methods are well known to those of ordinary skill in the art.

[00142] A denim fabric was subjected to a singeing treatment, a skewing treatment and a preshrinking treatment. Then, a thickened aqueous solution comprising an acid and a nitrate compound was applied to the surface.

[00143] A denim fabric was subjected to a singeing treatment, a skewing treatment, a preshrinking treatment and a desizing treatment. Then, a thickened aqueous solution comprising an acid and a nitrate compound was applied to the surface by printing.

[00144] A denim fabric was subjected to a singeing treatment, a skewing treatment, a preshrinking treatment and a desizing treatment. Then, an aqueous solution comprising an acid compound was applied by immersion and dried. The treated fabric is sewed to a garment and a nitrate salt containing solution is applied by spray to the garment.

[00145] A denim fabric was subjected to a singeing treatment, a skewing treatment, a preshrinking treatment and a desizing treatment. Then, an aqueous solution comprising an acid catalyst compound is applied to the surface by kiss-roll and dried. The treated fabric is sewed to a garment and a nitrate containing solution is applied by spray to the garment.

[00146] A denim fabric was subjected to a singeing treatment, a skewing treatment, a preshrinking treatment and a desizing treatment. Then, an aqueous solution comprising a nitrate compound is applied by immersion and dried. The treated fabric is sewed to a garment and an acid compound containing solution is applied by spray to the garment.

[00147] The color changing effect in such pretreated denim fabrics is then generated with irradiation, e.g. by a laser treatment (e.g. as disclosed in US2016263928, US2016060807, US2015343568, US2015298253, US2015121965, and US2012263904).

[00148] A denim fabric was subjected to a singeing treatment, a skewing treatment and a preshrinking treatment. Then, an aqueous solution comprising an acid and a nitrate compound is applied by immersing or only to the surface (e.g. kiss roll, knife application, foaming, etc.). The effect is generated during a subsequent laser treatment.

[00149] A denim fabric was subjected to a singeing treatment, a skewing treatment, a preshrinking treatment, an ozone treatment and/or a laser treatment. Then, an aqueous solution comprising an acid and a nitrate compound is applied by immersion or only to the surface (e.g. kiss roll, knife application, foaming, etc.). The effect is generated during a subsequent laser treatment.

[00150] A denim yarn is immersed in a solution comprising the acid and the nitrate. Subsequently the yarn is sized and woven to a fabric. The effect is generated during a subsequent laser treatment.

[00151] A solution comprising the acid and the nitrate is applied to denim yarn by a kiss roll, foaming or spray. Subsequently the yarn is sized and woven to a fabric. The effect is generated during a subsequent laser treatment.

[00152] A raw denim garment was abraded by laser or hand sanding to mark specific used look areas. Subsequently a solution containing nitrate and acid is sprayed or applied by brush or sponge on the abraded areas.

[00153] A raw denim garment was desized and dried. Subsequently a solution containing nitrate and acid is sprayed or applied by brush or sponge on the abraded areas.

[00154] A raw denim garment is used as it is, or desized, and/or stonewashed, and/or ozone treated, and/or enzyme washed and dried. Subsequently a solution containing nitrate and acid is sprayed or applied by brush or sponge on specific areas of the garment.

[00155] A raw denim garment is used as it is, or desized, and/or stonewashed, and/or ozone treated, and/or enzyme washed and dried. Subsequently a solution containing a nitrate salt is applied to the garment and dried. Subsequently a solution containing an acid catalyst is applied by brush or sponge on specific areas of the garment.

[00156] A raw denim garment is used as it is, or desized, and/or stonewashed or enzyme washed and dried. Subsequently a solution containing an acid catalyst is applied to the garment and dried. Subsequently a solution containing a nitrate salt is applied by brush or sponge on specific areas of the garment.

[00157] Pumice stones are soaked in a solution containing an acid and a nitrate salt and subsequently agitated with a denim garment in a tumbler.

[00158] A denim garment is wetted and placed together with a powder containing nitrate salt and acid catalyst (if needed together with a filler material like sand, perlite, etc.) in a bag and agitated until the effect is created.

[00159] The color changing effect in such pretreated denim fabrics is then generated with a laser treatment.

[00160] Examples according to [00141] to [00158] are subsequently rinsed with water, washed under acidic conditions (e.g. $\text{pH} \leq 5$) and/or basic conditions (e.g. $\text{pH} \geq 10$) at cold and/or warm conditions (e.g. 30-90°C) and a combination thereof.

[00161] Examples according to [00141] to [00158] are subsequently washed with methods known to the skilled person of the art, e.g. chlorine treatment, hydrogen peroxide treatment, potassium peroxide treatment, ozone treatment, enzyme (cellulose, laccase, peroxidase, etc.) treatment, stonewashing, glucose treatment, organo peroxide treatment, softening, tinting (adjusting the colour tone with dyestuffs), etc.

[00162] Examples according to [00141] to [00158] are previously washed with methods known to the skilled person of the art, e.g. chlorine treatment, hydrogen peroxide treatment, potassium peroxide treatment, ozone treatment, enzyme (cellulose, laccase, peroxidase, etc.) treatment, stonewashing, glucose treatment, organo peroxide treatment, scraping, lasering, ice-blasting, carbon dioxide blasting, sand blasting, etc.

[00163] Tables 1 to 7 depict compositions in aqueous solutions which are applied to fabrics.

Table 1

#	Nitrate Salt	[%]	Acid Catalyst	[%]	Acid	[%]	Time [h]
1	Mg(NO ₃) ₂ ·6H ₂ O	51.0	MgSO ₄	5.7	methanesulfonic acid	10.0	0.5
2	Mg(NO ₃) ₂ ·6H ₂ O	51.0	Ce(SO ₄) ₂	1.0	methanesulfonic acid	10.0	0.5
3	Mg(NO ₃) ₂ ·6H ₂ O	51.0	VOSO ₄	4.2	methanesulfonic acid	10.0	0.5
4	Mg(NO ₃) ₂ ·6H ₂ O	51.0	FeSO ₄	1.6	methanesulfonic acid	10.0	0.5
5	Mg(NO ₃) ₂ ·6H ₂ O	51.0	Fe ₂ (SO ₄) ₃	6.5	methanesulfonic acid	10.0	0.5
6	Mg(NO ₃) ₂ ·6H ₂ O	52.0			citric acid	30.0	4
7	Mg(NO ₃) ₂ ·6H ₂ O	34.8			tartaric acid	40.0	2
8	Mg(NO ₃) ₂ ·6H ₂ O	55.1			oxalic acid	5.0	0.5
9	Mg(NO ₃) ₂ ·6H ₂ O	51.0			methanesulfonic acid	10.0	0.5
10	Mg(NO ₃) ₂ ·6H ₂ O	51.0			nitric acid	6.5	0.5
11	Mg(NO ₃) ₂ ·6H ₂ O	51.0			methanesulfonic acid	10.0	0.5
12	Mg(NO ₃) ₂ ·6H ₂ O	51.0			HCl 25%	10.0	0.5
13	Mg(NO ₃) ₂ ·6H ₂ O	51.0	ZnCl ₂	3.3	methanesulfonic acid	10.0	0.5
14	Mg(NO ₃) ₂ ·6H ₂ O	51.0	FeCl ₃ 90%	9.7	methanesulfonic acid	10.0	0.5
15	Mg(NO ₃) ₂ ·6H ₂ O	51.0	CuCl ₂	4.1	methanesulfonic acid	10.0	0.5
16	Mg(NO ₃) ₂ ·6H ₂ O	51.0	FeCl ₂	4.8	methanesulfonic acid	10.0	0.5
17	Mg(NO ₃) ₂ ·6H ₂ O	51.0	AlCl ₃	3.2	methanesulfonic acid	10.0	0.5

#	Nitrate Salt	[%]	Acid Catalyst	[%]	Acid	[%]	Time [h]
18	Mg(NO ₃) ₂ ·6H ₂ O LiNO ₃	40.0 2.0			maleic acid	16.0	1
19	Mg(NO ₃) ₂ ·6H ₂ O LiNO ₃	57.0 2.9			H ₂ SO ₄	5.0	0.5
20	Mg(NO ₃) ₂ ·6H ₂ O LiNO ₃	51.0 2.6			HCl 25%	15.0	0.5
21	Mg(NO ₃) ₂ ·6H ₂ O LiNO ₃	30.0 1.5			tartaric acid	30.0	3
22	Mg(NO ₃) ₂ ·6H ₂ O LiNO ₃	60.0 3.0			H ₂ SO ₄ 98%	1.0	0.5
23	LiNO ₃	27.9			methanesulfonic acid	10.0	0.5
24	Al(NO ₃) ₃	50.5			methanesulfonic acid	10.0	0.5
25	Ca(NO ₃) ₂	47.7			methanesulfonic acid	10.0	0.5
26	Fe(NO ₃) ₃ ·9H ₂ O	54.0			methanesulfonic acid	10.0	0.5
27	Cu(NO ₃) ₂	48.0			methanesulfonic acid	10.0	0.5
28	Zn(NO ₃) ₂	60.0			methanesulfonic acid	10.0	0.5
29	KNO ₃	40.0			methanesulfonic acid	10.0	0.5
30	LiNO ₃	13.9			methanesulfonic acid	10.0	0.5
31	KNO ₃	20.0			methanesulfonic acid	10.0	0.5
32	Fe(NO ₃) ₃ ·9H ₂ O	40.0			methanesulfonic acid	10.0	0.5

#	Nitrate Salt	[%]	Acid Catalyst	[%]	Acid	[%]	Thickener	Temp	Time
								[°C]	[min]
33	(NH ₄) ₂ Ce(NO ₃) ₆	36.0			methanesulfonic acid	10.0	xanthan gum	50	20
34	Co(NO ₃) ₂ ·6H ₂ O	58.0			methanesulfonic acid	10.0	xanthan gum	50	20
35	Al(NO ₃) ₃ ·9H ₂ O	30.0			citric acid	25.0	xanthan gum	50	20
36	Mg(NO ₃) ₂ ·6H ₂ O	63.0			methanesulfonic acid	10.0	xanthan gum	50	20
Table 2									
#	Mg(NO ₃) ₂	+ Nitrate Salt	Acid	Acid	Acid	Acid	Thickener	Temp	Time
37	25	Al(NO ₃) ₃ ·9H ₂ O	5				xanthan gum	50	20
38	25	Al(NO ₃) ₃ ·9H ₂ O	4				xanthan gum	50	20
39	25	Al(NO ₃) ₃ ·9H ₂ O	3				xanthan gum	50	20
40	25	Al(NO ₃) ₃ ·9H ₂ O	2				xanthan gum	50	20
41	25	Al(NO ₃) ₃ ·9H ₂ O	1				xanthan gum	50	20
42	25	Al(NO ₃) ₃ ·9H ₂ O	0.1				xanthan gum	50	20
43	25	Al(NO ₃) ₃ ·9H ₂ O	45					60	20
44		Al(NO ₃) ₃ ·9H ₂ O	40					80	20
45		Al(NO ₃) ₃ ·9H ₂ O	35					80	20
46		Al(NO ₃) ₃ ·9H ₂ O	30					80	20
47		Al(NO ₃) ₃ ·9H ₂ O	25					80	20
48		Al(NO ₃) ₃ ·9H ₂ O	20					80	20
49		Al(NO ₃) ₃ ·9H ₂ O	18					80	20
				tartaric acid	1				

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	+ Nitrate Salt [%]	Acid Catalyst [%]	Acid [%]	Additive [%]	Thickener [%]	Temp [°C]	Time [min]
50	70		CaCl ₂ 2				20	20
51	70		ZnCl ₂ 2				20	20
52	70		NaCl 2				20	20
53	70		KCl 2				20	20
54	70		LiCl 2				20	20
55	70		SrCl ₂ 2				20	20
56	70		MgCl ₂ 2				20	20
57	70		(NH ₄) ₂ SO ₄ 2				20	20
58	70		CuSO ₄ 2				20	20
59	70		Li ₂ SO ₄ 2				20	20
60	70		NH ₄ Al(SO ₄) ₂ 2				20	20
61	70		KAl(SO ₄) ₂ 2				20	20
62	70		FeSO ₄ 2				20	20
63			Ce(SO ₄) ₂ 2				20	20
64	20	Al(NO ₃) ₃ ·9H ₂ O 4			Zn(NO ₃) ₂ ·6H ₂ O 0.05	xanthan gum 0.15	60	20
65	25	Fe(NO ₃) ₂ ·6H ₂ O 1		tartaric acid 4			80	10
66	30	Fe(NO ₃) ₂ ·6H ₂ O 0.01		tartaric acid 1			80	20
67		LiNO ₃ 30					80	20
68	35		CaCl ₂ 2	citric acid 10			60	20
69	35		ZnCl ₂ 2	citric acid 10			60	20
70	35		NaCl 2	citric acid 10			60	20

#	Mg(NO ₃) ₂ -6H ₂ O [%]	+ Nitrate Salt [%]	Acid Catalyst [%]	Acid [%]	Additive [%]	Thickener [%]	Temp [°C]	Time [min]
71	35		KCl	2 citric acid	10		60	20
72	35		LiCl	2 citric acid	10		60	20
73	35		SrCl ₂	2 citric acid	10		60	20
74	35		MgCl ₂	2 citric acid	10		60	20
75	35		(NH ₄) ₂ SO ₄	2 citric acid	10		60	20
76	35		CuSO ₄	2 citric acid	10		60	20
77	35		Li ₂ SO ₄	2 citric acid	10		60	20
78	35		NH ₄ Al(SO ₄) ₂	2 citric acid	10		60	20
79	35		KAl(SO ₄) ₂	2 citric acid	10		60	20
80	35		FeSO ₄	2 citric acid	10		60	20
81	35		Ce(SO ₄) ₂	2 citric acid	10		60	20
82	35		CaCl ₂	2 tartaric acid	4		60	20
83	35		ZnCl ₂	2 tartaric acid	4		60	20
84	35		NaCl	2 tartaric acid	4		60	20
85	35		KCl	2 tartaric acid	4		60	20
86	35		LiCl	2 tartaric acid	4		60	20
87	35		SrCl ₂	2 tartaric acid	4		60	20
88	35		MgCl ₂	2 tartaric acid	4		60	20
89	35		(NH ₄) ₂ SO ₄	2 tartaric acid	4		60	20
90	35		CuSO ₄	2 tartaric acid	4		60	20

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	+ Nitrate Salt [%]	Acid Catalyst [%]	Acid [%]	Additive [%]	Thickener [%]	Temp [°C]	Time [min]
91	35		Li ₂ SO ₄	2 tartaric acid	4		60	20
92	35		NH ₄ Al(SO ₄) ₂	2 tartaric acid	4		60	20
93	35		KAl(SO ₄) ₂	2 tartaric acid	4		60	20
94	35		FeSO ₄	2 tartaric acid	4		60	20
95	35		Ce(SO ₄) ₂	2 tartaric acid	4		60	20
96	25			tartaric acid	5 Zn(NO ₃) ₂ ·6H ₂ O	0.09	60	20

Table 3

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	+ Nitrate Salt	[%]	Acid	[%]	Addition	[%]	Thickener	[%]	Temp [°C]	Time [min]
97	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	tartaric acid	2					60	20
98	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	malonic acid	2					60	20
99	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	citric acid	2					60	20
100	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	maleic acid	2					60	20
101	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	methanesulfonic acid	5					60	20
102	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	methanesulfonic acid	10					60	20
103	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	tartaric acid	2	DMSO	1			60	20
104	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	tartaric acid	2	LiNO ₃	1			60	20
105	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	tartaric acid	2	triethanolamine	5			60	20

Table 4

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	Acid Catalyst	[%]	Acid	[%]	Temp [°C]	Time [min]
106	35	KAl(SO ₄) ₂ ·12H ₂ O LiCl	5 2.5	tartaric acid	2	60	20
107	35	KAl(SO ₄) ₂ ·12H ₂ O LiCl	5 1	tartaric acid	2	60	20
108	35	KAl(SO ₄) ₂ ·12H ₂ O LiCl	5 0.5	tartaric acid	2	60	20
109	35	KAl(SO ₄) ₂ ·12H ₂ O LiCl	5 0.1	tartaric acid	2	60	20
110	35	KAl(SO ₄) ₂ ·12H ₂ O	5	malonic acid	2	60	20
111	35	KAl(SO ₄) ₂ ·12H ₂ O	5	citric acid	2	60	20
112	35	KAl(SO ₄) ₂ ·12H ₂ O	5	maleic acid	2	60	20
113	35	KAl(SO ₄) ₂ ·12H ₂ O	5	lactic acid	2	60	20
114	35	KAl(SO ₄) ₂ ·12H ₂ O	5	oxalic acid	2	60	20

Table 5

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	Acid Catalyst	Acid [%]	Additive [%]	Temp [°C]	Time [min]
115	35	KAl(SO ₄) ₂ ·12H ₂ O	5 acetic acid	2	60	20
116	35	KAl(SO ₄) ₂ ·12H ₂ O	5 phosphoric acid	1	60	20
117	70	KAl(SO ₄) ₂ ·12H ₂ O	5 hydrochloric acid	3.6	60	20
118	35	KAl(SO ₄) ₂ ·12H ₂ O	5 sulphuric acid	4.5	60	20
119	35	KAl(SO ₄) ₂ ·12H ₂ O	5 salpetric acid	1.5	60	20
120	35	KAl(SO ₄) ₂ ·12H ₂ O	5 tartaric acid	2 Dispersoko ICP 100 CO	0.01 60	20
121	35	KAl(SO ₄) ₂ ·12H ₂ O	5 tartaric acid	2 Dispersoko ICP 100 PL	0.01 60	20
122	35	KAl(SO ₄) ₂ ·12H ₂ O	5 tartaric acid	2 polysorbate 20	0.1 60	20
123	35	KAl(SO ₄) ₂ ·12H ₂ O	5 tartaric acid	2 Nofome AF	0.1 60	20

Table 6

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	Nitrate Salt	[%]	Acid Catalyst	[%]	Acid	[%]	Additive	[%]	Temp [°C]	Time [min]
124	35			KAl(SO ₄) ₂ ·12H ₂ O	5	tartaric acid	2	Setamol Disperse WS	0.1	60	20
125	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05			tartaric acid	2	Methyl red	0.01	60	20
126	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05			tartaric acid	2	Chromene Red	0.005	60	20
127	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05			tartaric acid	2	Chromene Red	0.01	60	20
128	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05			tartaric acid	2	Chromene Red	0.015	60	20
129	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05			tartaric acid	2	Chromene Red	0.02	60	20
130	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05			tartaric acid	2	Chromene Red	0.025	60	20
131	35			KAl(SO ₄) ₂ ·12H ₂ O	5	tartaric acid	2	Methyl red	0.01	60	20
132	35			KAl(SO ₄) ₂ ·12H ₂ O	5	tartaric acid	2	Chromene Red	0.005	60	20

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	Nitrate Salt	[%]	Acid Catalyst	[%]	Acid	[%]	Additive	[%]	Temp [°C]	Time [min]
133	35			KAl(SO ₄) ₂ ·12H ₂ O	5	tartaric acid	2	Chromene Red	0.01	60	20
Table 7											
#	Mg(NO ₃) ₂ ·6H ₂ O [%]	Acid Catalyst / Nitrate Salt	[%]	Acid	[%]	Additive	[%]	Thickener	[%]	Temp [°C]	Time [min]
134	35	KAl(SO ₄) ₂ ·12H ₂ O	5	tartaric acid	2	Chromene Red	0.015			60	20
135	35	KAl(SO ₄) ₂ ·12H ₂ O	5	tartaric acid	2	Chromene Red	0.02			60	20
136	35	KAl(SO ₄) ₂ ·12H ₂ O	5	tartaric acid	2	Chromene Red	0.025			60	20
137	35					monosodium phosphate	2			60	20
138	35					monosodium phosphate	5			60	20
139	35					monopotassium phosphate	2			60	20
140	35					monopotassium phosphate	5			60	20
141	35									60	20

#	Mg(NO ₃) ₂ ·6H ₂ O [%]	Acid Catalyst / Nitrate Salt	[%]	Acid	[%]	Additive	[%]	Thickener	[%]	Temp [°C]	Time [min]
142	35					disodium pyrophosphate	5			60	20
143	25					disodium pyrophosphate	5			60	20
144	20					disodium pyrophosphate	5			60	20
145	15					disodium pyrophosphate	5			60	20
146	35					disodium pyrophosphate	5			45	20
147	20					disodium pyrophosphate	5			45	20
148	35			tartaric acid	1	Tetranatrium-diphosphat	1.5			60	20
149	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	tartaric acid	2	Trilon M	0.01			60	20
150	26.6	Zn(NO ₃) ₂ ·6H ₂ O	0.05	tartaric acid	2	Dissolvine GL 38	0.01			60	20

Claims

1. A method for increasing the color of a dyed textile material comprising the steps of:
 - a. pretreating the textile material with at least one nitrate salt and optionally an acid catalyst,
 - b. drying the pretreated fabric at temperatures less than 60 °C,
 - c. applying a laser beam to the textile material to generate NO_x compounds which attack the dye, and thereby
 - d. creating a color value change.
2. The method according to claim 1, wherein the nitrate salt is an organic or inorganic nitrate salt.
3. The method according to claim 2, wherein the inorganic nitrate salt is selected from the group consisting of Mg(NO₃)₂, KNO₃, LiNO₃, Al(NO₃)₃, Ca(NO₃)₂, Fe(NO₃)₃, Cu(NO₃)₂, Co(NO₃)₂, (NH₄)₂Ce(NO₃)₆, NaNO₃, RbNO₃, CsNO₃, Sr(NO₃)₂, Ba(NO₃)₂, Sc(NO₃)₃, Ti(NO₃)₄, Zr(NO₃)₄, VO(NO₃)₃, Cr(NO₃)₃, Mn(NO₃)₂, Co(NO₃)₂, Co(NO₃)₃, Ni(NO₃)₂, Pd(NO₃)₂, AgNO₃, Cd(NO₃)₂, Hg₂(NO₃)₂, Hg(NO₃)₂, [B(NO₃)₄]⁻, Ga(NO₃)₃, Tl(NO₃)₃, Pb(NO₃)₂, Bi(NO₃)₃, FNO₃, ClNO₃, Xe(NO₃)₂, Ce(NO₃)₃, Ce(NO₃)₄, Gd(NO₃)₃.
4. The method according to 3, wherein the nitrate salt is Mg(NO₃)₂, KNO₃, LiNO₃, NaNO₃, Al(NO₃)₃, Ca(NO₃)₂, Fe(NO₃)₃, Cu(NO₃)₂, Zn(NO₃)₂, Co(NO₃)₂, or (NH₄)₂Ce(NO₃)₆.
5. The method according to any of claims 1 to 4, wherein the nitrate salt is applied in solution, wet or dry form.
6. The method according to any one of claims 1 to 5, wherein the acid catalyst is selected from the group consisting of organic or inorganic compounds, i.e. organic or inorganic chlorides, sulfates, phosphates, borates, fluorides, acid forming esters, amino acid hydrochlorides, and Lewis acid chlorides.
7. The method according to claim 6, wherein the acid catalyst is selected from the group consisting of methanesulfonic acid, citric acid, tartaric acid, oxalic acid, toluenesulfonic acid, succinic acid, maleic acid, malic acid, sulfuric acid, hydrochloric acid, phosphoric acid, salicylic acid and mixtures thereof.
8. The method according to claim 6, wherein the Lewis acid chloride is ferric chloride, zinc chloride, lithium chloride, copper chloride, magnesium chloride or aluminum chloride and a sulfate as magnesium sulfate, iron sulfate, iron sulfate, cerium

sulfate, vanadium sulfate, copper sulfate, lithium sulfate, aluminum sulfate, potassium aluminum sulfate, ammonium aluminum sulfate, sodium sulfate, sodium hydrogen sulfate, zinc sulfate and manganese sulfate, and the phosphate is a monosodium phosphate, disodium phosphate, monopotassium phosphate, dipotassium phosphate, monomagnesium phosphate, dimagnesium phosphate, trimagnesium phosphate, ammonium polyphosphate, monoammonium phosphate, diammonium phosphate, monocalcium phosphate, dicalcium phosphate, disodium pyrophosphate, trisodium pyrophosphate, tetrasodium pyrophosphate, sodium triphosphate, pentapotassium triphosphate.

9. The method according to any one of claims 1 to 8, wherein the acid catalyst is provided as a buffered substance.
10. The method according to any one of claims 6 to 8, wherein the acid catalyst is capsuled.
11. The method according to any one of claims 1 to 9, wherein the treatment is carried out by a temperature of below 65 °C, or at a temperature of below 90 °C, or at higher temperature where applicable, if the acid catalyst decreases the activation temperature in comparison to the pure nitrate.
12. The method according to claim 1, wherein the textile material is treated with an aqueous solution comprising at least one nitrate salt which is activated by an acid catalyst, wherein the treatment is carried out until the desired color change is achieved.
13. The method according to claim 12, wherein said aqueous solution comprises $\text{Mg}(\text{NO}_3)_2$, another nitrate compound (e.g. $\text{Al}(\text{NO}_3)_3$) and an acid, e.g. tartaric acid.
14. The method according to claim 12, wherein said aqueous solution comprises $\text{Al}(\text{NO}_3)_3$ and toluenesulfonic acid.
15. The method according to any one of claims 12 to 14, wherein the pH of the aqueous solution is higher than 2.
16. The method according to any of claims 1 to 15, wherein the pretreatment is carried out at a temperature of about 10 to 90 °C, or at a temperature of about 10 to 60 °C, or at a temperature of about 10 to 50 °C or at room temperature.
17. The method according to any of claims 1 to 16, wherein the pretreatment step is carried out in the presence of a sulfate and/or chloride compound.

18. The method according to any of claims 1 to 17, wherein optionally an auxiliary agent is used.
19. The method according to claim 18, wherein said auxiliary agent is selected from the group consisting of a nitrate, softener, brightening agent, plastic, silicate, amorphous or crystalline silicon dioxide, a thickening agent, dyestuff used as a marker dye, a wetting agent, a complexing agent, a dispersing agent, and a buffer solution derived from the salt of an acid and the corresponding acid.
20. The method according to any one of claims 1 to 19, wherein the fabric is dyed with a sulphur dye, reactive dye, direct dye, VAT dye, basic dye, pigment dye, a natural dye or a mixture thereof.
21. The method according to any one of claims 1 to 20, wherein the ΔL value between the untreated and treated part is greater than 2 (L stands for the lightness in the CIE 1976 Lab color space).
22. The method according to any one of claims 1 to 20, wherein the laser beam is applied to the fabric to change the color intensity to value ranges of L from 15-40 to 30-60, or from 15-30 to 30-60.
23. The method according to any of claims 1 to 20, wherein Lab color space lightness value ranges for L of from 20 to 60 are achieved by laser treatment.
24. The method according to any of claims 1 to 20 which increases the Lab color space lightness value L of the denim garment by 2 points.
25. An article obtained according to any of claims 1-24.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/080371

A. CLASSIFICATION OF SUBJECT MATTER INV. D06P5/13 D06P5/15 D06M10/00 D06M11/58 ADD.		
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) D06P D06B D06M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 567 207 A (LOCKMAN WILLIAM J [US] ET AL) 22 October 1996 (1996-10-22) cited in the application the whole document	1-25
A	GB 469 091 A (COLORAY CORP) 19 July 1937 (1937-07-19) page 1, lines 63-74 page 1, lines 86-89 page 2, lines 4-9 page 2, lines 21-38 page 3, lines 83-87 page 5, lines 15-20 Examples: Solution No. 1 claims 4, 15-17	1-25
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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		Date of mailing of the international search report
22 February 2017		16/03/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Rella, Giulia

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/080371

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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