

# UNITED STATES PATENT OFFICE.

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## PROCESS OF BLEACHING.

**SPECIFICATION** forming part of Letters Patent No. 534,450, dated February 19, 1895.

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*To all whom it may concern:*

Be it known that we, JOHN CLAPHAM, a subject of Her Majesty the Queen of Great Britain, residing at Bradford, in the county of York, England, JULES PICARD and CYPRIEN VILLEDIEU, citizens of the French Republic, residing at Paris, in said Republic, and WALTER WILLIAM LANCASTER LISHMAN, a subject of Her Majesty the Queen of Great Britain, residing at Bradford aforesaid, have invented a certain new and useful Improved Process of Bleaching and Decoloration; and we do hereby declare that the following is a full, clear, and exact description of the invention, that will enable others skilled in the art to which it appertains to use the same.

The following materials may be wholly or partially bleached as desired: No. 1, cotton in the raw or manufactured state; No. 2, linen in the raw or manufactured state; No. 3, flax in the raw or manufactured state; No. 4, hemp in the raw or manufactured state; No. 5, jute in the raw or manufactured state; No. 6, grasses in the raw or manufactured state; No. 7, straw in the raw or manufactured state, such as noils, yarns and pieces; No. 8, paper pulp such as rag pulp, straw pulp, wood pulp; No. 9, silk in the raw or manufactured state; No. 10, wool in the raw or manufactured state; No. 11, hairs in the raw or manufactured state, such as noils, yarns and pieces; No. 12, feathers; No. 13, sponges; No. 14, horn; No. 15, ivory; No. 16, wood; No. 17, leather.

To effect the bleaching of Nos. 1, 2, 3, 4, namely, cotton, linen, flax, and hemp, we proceed in the following manner: The substances or materials mentioned are first saturated thoroughly by the processes now in vogue in the different dyehouses and bleachworks; which saturation is generally accomplished by treating with boiling water (or boiling water containing a quantity of alkali, such as soda ash, soda crystals, or the like), so as to remove any grease or foreign matter which is capable of being removed thereby, or to soften the same. Of such processes, we prefer keir boiling whenever possible; as that principle of boiling insures the removal of grease and foreign matter; which not only allows a greater bril-

liancy of white to be produced, but also reduces the quantity of ingredients used in this process; and, therefore, also reduces the cost. After washing, we take any or all the materials or substances under operation and pass them for one, two, or more minutes through a bath which we will call bath 1. This contains water and a quantity of sulfonated or soluble oil (as olein oil). It is preferable to have this bath on the acid side. This may be produced by adding if required a little acid (sulfuric acid preferred) to the bath; or instead of the sulfonated or soluble oil a quantity of soap, or glycerine, or glycerine and soap, combined, or glucose, or glucose and soap. The temperature of this bath may be varied according to the discretion of the bleacher. Under ordinary circumstances, a suitable strength of solution is from one per cent. to five per cent., and temperature from cold to about 30° to 40° centigrade. After passing through this bath, the desired length of time (for which we find one-half to one, two, or more minutes for cotton; and one, two or more minutes for linen, flax, and hemp, according to the thickness of the material or substance being treated is suitable). The material or substance is then squeezed or wrung out and washed in a bath which we will call bath 2. This bath contains water; and, when sulfonated oil has been used, it is better also to add a little acid to the water to acidulate it slightly, after which the material is squeezed or wrung out, and is then passed through bath 3. This bath is made up of water at variable temperatures (a suitable temperature being 25° to 30° centigrade, or thereabout, for cotton; while for linen, flax, and hemp, it is better to keep the bath cooler, say at 10° centigrade), and a manganate or permanganate salt (as permanganate of potash) or soda, but preferably permanganate of potash, in quantity sufficient for the quantity of material or substance to be treated. The material or substance to be bleached should, if possible, be kept slowly moving and the bath should be kept at a standard strength by adding from time to time the amount of manganate or permanganate requisite for same. A very suitable strength of solution is

a one per cent. solution. A little inorganic acid as sulfuric acid, and an amount of alkaline chlorid, such as common salt, or sulfate, such as Glauber's salt (sodium sulfate), which should be equal to about half the weight of the manganate or permanganate used to check the oxidizing action of the manganate salt, may with advantage be added. After passing for one, two, or more minutes through this bath or until the material or substance has assumed a dark brown color, it is squeezed or wrung out, and then passed through a bath which we will call bath 3<sup>a</sup>. This bath contains water, to which a little acid has been added (preferably the same acid as used in bath 3 to acidulate). The material is then squeezed or wrung out, and is then passed through bath 4. This bath is made up of water, at any temperature from cold to boiling, and a sufficient quantity, for amount of material, or substance to be treated, of any of the alkaline or metallic sulfites, hydrosulfites or bisulfites (as ammonium bisulfite, sodium bisulfite or potassium bisulfite) but preferably sodium bisulfite or ammonium bisulfite, and a little acid, such as sulfuric acid. To facilitate the liberation of sulfurous acid also, a little starch and a little metallic chlorid may be used, or sulfate (as magnesium sulfate or magnesium chlorid), and also a little oxalic acid, but these three latter are optional. The bath may also be made up of water and peroxid of hydrogen, or peroxid of barium, or of sodium or of potassium, and a little acid; or the bath may be made up of water, acidulated with a little acid and a little salt, through which a current of electricity is allowed to pass; or the bath may contain water, a little acid, and a chlorid of the alkalies or metals, as potassium or sodium chlorite or hypochlorite; or the bath may be made up of water, a little acid, and hydrosulfite of the alkalis, or metals. After being passed for one, two, or more minutes or until the requisite degree of whiteness has been produced it is wrung out and washed off by passing through a bath which we will call bath 5. This contains water, after passing through which the material is then squeezed out, and (should the bisulfite, hydrosulfite or chlorite method have been used) is then passed through bath 6. This is made up of water and acid, say sulfuric acid (or preferably for some fibers, hydrochloric acid, oxalic, or acetic acids), of a suitable strength according to the nature of the material being treated. This is to insure the liberation of the sulfurous or chlorous acids which may be present. After being squeezed out from bath 5 after washing from bath 4 it is then squeezed or wrung out and passed through bath 7. This contains water to remove any trace of free acid which may remain from bath 6. Should the peroxid or electrical process have been used, it is not necessary to pass the material or substance through baths 6 and 7. Should the desired shade or quality of white

not be obtained the first time, this process may be repeated; but it will only in a few cases be found necessary where the substance or material is of a very dark color. The material or substance is now finished and may be treated by any means now in vogue, as soaping, drying, spinning, winding, weaving, and dyeing, as desired.

To effect the bleaching of jute and grasses such as china grasses we may make the following alterations from the foregoing, namely:—after the boiling or saturating process aforesaid, we treat the material or substance in a bath made up of water, say at 40° centigrade, and containing about five per cent. of bichromate of soda or potash, and a little acid, such as sulfuric acid. The operation on materials numbered 5 and 6 is optional; or the process under materials numbered 1, 2, 3, 4 is alone followed out. Before drying, in the case of materials numbered 5 and 6, also materials numbered 1, 2, 3, 4, a distinct advantage is gained, especially if the material is in the raw or unmanufactured state, by passing it through a bath which we call bath 8. This contains a quantity of, say one per cent. to three per cent. of olein or soluble oil, or an emulsion of oil or oils (in this case it is preferable to have the solution neutral). This bath makes the material or substance more easy to work up.

To effect the bleaching of material numbered 7 (straws),—after the saturating process, the straw is allowed to stand in a bath made up of water (say at 15° centigrade) and a quantity sufficient for the amount of material taken (say three per cent.) of any of the manganates or permanganates of the metals, and a little acid, for say half an hour. It is then squeezed out; washed in a bath with water acidulated with a little acid, as named under bath 3<sup>a</sup>; and then squeezed out and passed into a bath which may be made up of any of the ingredients named under bath 4. In the process given for the materials numbered 1, 2, 3, and 4 an alkaline chlorite, such as sodium hypochlorite is preferably used. The material is allowed to stand in this bath several hours, or until the requisite degree of whiteness is produced, and it is then treated as materials numbered 1, 2, 3, 4 are treated by passing through baths 5, 6, and 7.

To effect the bleaching of the materials numbered 9, 10, 11, 12, namely, silk, wool, hairs and feathers, as tussah silks, organzine silks, sheep's wool, alpaca wool, mohair, camel's hair, and ostrich feathers, we proceed as follows: After passing through the process known in the case of wool and hairs as "scouring," and in the case of silks and feathers as "discharging," the materials or substances are treated in the following baths: Bath 1, which we term the oil bath, made up of water and olein oil, or water and soap or glycerine, or any of the other ingredients aforesaid named under bath 1 at a temperature of from 45° to

110

50° centigrade or cooler, preferably or at as low as 20° centigrade. The material is then passed through bath 2 of water, to which a little acid has been added, should olein oil have been used. This bath is for the purpose of washing the material. The material is then passed for a short time through bath 3, which may be composed of water and any of the manganese salts of the alkali metals, or alkaline earths, or oxids of manganese, or the manganates or permanganates of the metals, and with or without a little acid. If acid is used it is preferably an organic acid as acetic acid. The material is then squeezed or wrung out and passed through slightly acidulated water to wash off, then squeezed or wrung out and then passed through bath 4. This in the case of feathers and silk, is best cold, and in the case of wool and hairs, cold to moderately warm, say at 20° centigrade, but preferably cold. This bath is made up of water, acid, and sulfite, bisulfite or hydrosulfite of the metals, or alkalies; or water, acid, and peroxid of hydrogen, barium, sodium, or potassium; or water, and acid, and salt, with a current of electricity passing through it. In this case either bisulfite of ammonia or peroxid of hydrogen are most suitable. The material is then passed through bath 5. This consists of water to wash off the material, which is then passed through baths 6 and 7, if necessary, as described under process given for substances numbered 1, 2, 3, 4.

In bleaching tussah silk, if desired, it may be passed through a bath of acid and bichromate of soda or potash, to reduce some of the coloring principle.

In the production of certain tints of white, this is accomplished by passing the substance or material through a bath containing a little blue, such as are used today in the sulfur process, as neutral extract of indigo, indigo carmine, &c. This bath containing blue matter may be employed after bath 1, or after bath 3; or, if after bath 3, should too much blue have been used, the substance or material should be passed again through bath 3 rapidly before entering baths 3<sup>a</sup> and 4.

To effect the bleaching of the material numbered 13 (sponges) we proceed in exactly the same manner as described for the materials numbered 9, 10, 11, 12 keeping the temperature of the baths low.

To effect the bleaching of the materials numbered 14, 15, 16, and 17, (horn, ivory, wood, leather,) we proceed in exactly the same manner as described under the process given for the materials numbered 9, 10, 11, and 12, keeping the temperature low. In the bleaching of these materials, the process has to be repeated one, two, or more times to obtain good shades or degrees of whiteness.

To effect the bleaching of the material numbered 8 paper pulp (as rag pulp, straw pulp, wood pulp), after the pulp is made ready to be passed through the bleaching process as

it is made or prepared at present, we proceed in exactly the same manner as described with reference to the materials numbered 1, 2, 3, and 4, keeping the baths cold, at about 10° centigrade.

The foregoing processes may be used for the discharging of coloring or the decoloration of matters, such as dyes, from any of the named substances or materials. In the case of dyed tissues, it is advisable, in some cases, to treat with a bath of bichromate of soda or potash, and a little acid. Before proceeding with the process, it is also advisable to add a little oxalic acid to bath 4 described with reference to its use for the materials numbered 1, 2, 3, and 4 the process being exactly the same as described in this connection but with the foregoing alteration.

Our object is not only to produce a better or a cheaper white, but also to reduce the risk of injuring the material or substance, as is done in the present process of bleaching, and also to lessen the amount of labor entailed.

The following methods and appliances are suitable for working the above materials or substances.

It will be seen that the main characteristic features of our invention are in the preliminary treatment of the material to be bleached by a sulfonated or soluble oil such for example as olein oil. This substance employed in such a manner as is described herein has a very remarkable protective action, forming or depositing what may be termed a shield, by which the fiber submitted to treatment is preserved from the destructive power of the oxidizing agent, while at the same time the natural color, or the coloring matter with which the fiber is stained, can be freely oxidized; and it also acts as a mordant, by which fibers, such as herein referred to, are enabled to take up a larger quantity of permanganate of potash than it otherwise could absorb. Thus the bleaching agent is enabled to reach the innermost parts of the fiber, and to operate upon the coloring matter in situations in which it would, without this preliminary treatment, be comparatively inaccessible; by which means the bleaching operation is facilitated, while at the same time the protective action of the oil defends the fiber itself from structural injury. Furthermore by confining the action of the permanganate to the coloring matters this oil effects an appreciable economy of the bleaching agent.

The remaining steps of the process hereinbefore described are mainly directed to the two following ends: (a) to the reduction of the manganates permanganates, &c., employed in the process by the processes herein described, into "colorless," and also as far as possible soluble salts (such as the sulfates of ammonium, sodium, potassium, &c.) which salts will thereby be rendered capable of removal by washing, &c. (b) the extraction of such constituents, for example manganese, as

may be profitably recovered from the residual solution.

We claim as new—

1. The process of bleaching and decoloring fibers and the like which consists in treating the same in a bath containing a substance having a protective action on the fibers, such as a sulfonated or soluble oil; then in a bath containing a manganate, or permanganate salt; then in a bath having a bleaching or whitening action; and then washing same, substantially as described.
2. The process of bleaching and decoloring fibers and the like, which consists in treating the same in a bath containing a sulfonated or soluble oil, such as olein oil; then in a bath containing a manganate or permanganate salt; then in a bath having a bleaching or whitening action; then washing same; then treating in a bath of water and acid to insure the liberation of any sulfurous acid; and then washing same, to remove the acid from the previous bath, substantially as described.
3. The process of bleaching and decoloring fibers and the like, which consists in treating the same in a bath containing a sulfonated or soluble oil, such as olein oil; then in a bath containing a manganate or permanganate salt; in a bath of acidulated water; in a bath having a bleaching or whitening action; and finally washing same, the various steps being carried out in the orders and for the purposes described.
4. The process of bleaching and decoloring fibers and the like, which consists in treating the same in a bath containing a sulfonated or soluble oil, such as olein oil; then treating in a bath containing a manganate or permanganate salt; then in a bath having a bleaching

or whitening action; then washing same; and then treating in a bath containing olein or soluble oil as an emulsion substantially as described.

5. The process of bleaching and decoloring fibers and the like which consists in treating the same in a bath containing a sulfonated or soluble oil, such as olein oil; in baths of acidulated water; in a bath containing a manganate or permanganate salt; in a bath having a bleaching or whitening action; in wash baths; and finally treating in a bath containing olein or soluble oil, as an emulsion, the various steps being carried out in the orders and for the purposes described.

In testimony whereof we affix our signatures each in the presence of two witnesses.

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