UNITED STATES PATENT OFFICE.

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PROCESS OF DYEING BLACK.

SPECIFICATION forming part of Letters Patent No. 493,286, dated March 14, 1893.

Application filed August 28, 1891. Serial No. 404,008. (No specimens.) Patented in France March 31, 1888, No. 189,733; in Belgium October 10, 1888, No. 83,551; in Germany October 13, 1888, No. 48,595; in England November 24, 1888, No. 17,094; in Austria-Hungary June 5, 1889, No. 882 and No. 10,799, and in Italy August 26, 1889, XXIII, 26,049, LI, 220.

To all whom it may concern:

Be it known that I, CHARLES FRANÇOIS XAVIER NOROY, chemist, of 223 Faubourg St. Honoré, Paris, in the Republic of France, have invented a new or Improved Dyeing Material and Method of Employing the Same, (for which I have obtained Letters Patent of France for fifteen years, No. 189,733, dated March 31, 1888; of Belgium, No. 83,551, dated October 10, 1888; of Great Britain, No. 17,094, dated November 24, 1888; of Germany, No. 48,595, dated October 13, 1888; of Austria-Hungary, No. 882 and No. 10,799, dated June 5, 1889, and of Italy, No. 26,049/220, Vol. XXIII/LI, dated August 26, 1889;) and I do hereby declare that the following is a full and exact description thereof.

This invention relates to a new method of dyeing in black, which may be used alike for fabrics composed of a mixture of cotton and wool, for those composed of cotton only, or of wool only, as well as for animal fibrous-materials, and for skins of all kinds.

The novelty of this invention consists in dyeing in an alkaline medium, by means of a new product, which I call neutralized nitrated starch, and which possesses the property of holding in solution in an alkaline medium nearly all the oxides or salts, such as those of iron, copper, zinc, chromium, nickel, manganese, antimony, tin, arsenic, aluminium, magnesium, &c.

The advantage of dyeing in baths, which possess slight alkalinity without causticity is that there is no alteration in the wool or cotton, the oxides penetrating fully and quickly into the fibers, where they produce the coloring matter, that is to say the dye. With two baths I complete the process of dyeing. The first bath supplies the coloring matters, and the second one, which contains the several oxides in solution in the alkaline medium by the help of my new material, fixes them.

Composition of the baths and of neutralized nitrated starch.

First bath.—The first bath is composed of logwood and water, then of a certain quantity of any salt of copper, such as sulphate, nitrate, chloride, acetate, or pyrophosphate, &c. for example, and also a certain quantity of some suitable acid and, preferably, the common pyroligneous acid to be found in trade.

The second bath.—The second bath, called the fixing bath, is composed of a solution of several salts in the neutralized nitrated starch, which is neutralized and even slightly alkaline. Neutralized nitrated starch, which I have created, is a product which results from a first oxidizing reaction of nitric acid upon fecula, starch, flour (or generally upon cellulose and lignine). After this reaction, the product is neither soluble starch, such as defined by chemistry, nor tartaric acid, nor oxalic acid, as might be supposed, but that product which is produced between the first state of oxidation by nitric acid and one of the last of these states. Its mode of preparation is sufficient to specify it. One sees that it is starch from which a certain quantity of carbon and hydrogen has been taken, and to which a certain quantity of nitrogen has been added perhaps. An analysis as to the quantities of its elements would give the exact composition. This non-neutralized product was first designed under the name of nitrated starch, but when neutralized either by ammonia, soda, or potash, its name becomes neutralized nitrated starch. To obtain this product, this is how I proceed;—I put, in a porcelain, or emameled sheet-iron vessel, one kilo of fecula, or starch, &c., then I pour upon it two kilos of nitric acid of commerce, afterward I slightly heat the mixture. As soon as the starch is dissolved and the red vapors are about to be disengaged abundantly, I remove the vessel from the fire and allow the tumultuous reaction to proceed until no more vapor is given off. The liquid thus obtained is nitrated starch. I neutralize it by a solution of soda, potash, or ammonia, or by a carbonate of these alkalies. I have then obtained the neutralized nitrated starch, and thus with one kilo of fecula, two kilos of nitric acid, and a solution of one of the alkalies, I make four kilos of it. The neutralized nitrated starch or nitrated starch neutralized is, in this state of dilution, suitable for being put with the fixing mixtures.

Different fixing mixtures.—The second

bath, called the fixing-bath, may vary in its composition in any number of ways, for, any oxide or salt dissolved in neutralized nitrated starch makes a fixing mixture at once. I give here some examples of the composition of fixing mixtures. When diluted with water, each of these mixtures forms a second bath, the good effects of which have been seen, although there are some variations in the shades of black.

First. Neutralized nitrated starch, eighty; alum, twelve; sulphate of iron, twelve; sulphate of copper, six; bichromate of potash, fifty-five; six hundred or seven hundred grams of water for dissolving; some ammonia or solution of soda for neutralizing, after having been made slightly alkaline, then water enough to make one liter.

Second. Neutralized nitrated starch, eighty; alum, twelve; sulphate of iron, ten; sulphate of zinc, ten; bichromate of potash, fifty; six hundred or seven hundred grams of water for dissolving; ammonia or solution of soda for neutralizing, after having been made slightly alkaline, then water enough to make one liter.

Third. Neutralized nitrated starch, eighty; alum, twelve; sulphate of iron, ten; sulphate of copper, eight; bichromate of potash, fifty; six hundred or seven hundred grams of water for dissolving; ammonia or solution of soda for neutralizing, after having been made slightly alkaline, then water enough to make one liter.

Fourth. Neutralized nitrated starch, eighty; alum, twelve; chloride of manganesium, ten; sulphate of zinc, six; bichromate of potash, fifty; six hundred or seven hundred grams of water for dissolving; ammonia or solution of soda for neutralizing, after having been made slightly alkaline, then water enough to make one liter.

Fifth. Neutralized nitrated starch, eighty; alum, twelve; chloride of manganesium, ten; sulphate of copper, twelve; bichromate of potash, sixty; six hundred or seven hundred grams of water for dissolving; ammonia or solution of soda for neutralizing, after having been made slightly alkaline, then water enough to make one liter.

The quantities shown in the above formulas are for one kilo of stuff, and for one liter of mixture, as above shown, but this liter will be increased by water to fifteen or twenty times its volume, to make the fixing bath for the said one kilo of fabric.

The dye.—The first bath, for supplying, logwood to the fabrics, threads, &c., must contain ten to twelve grams of logwood per liter (dry extract of logwood). This is a bath, which, when once made, may be used indefinitely as it were, in putting in, after each operation, fresh quantities of logwood. To the logwood must be added a solution of any salt of copper, as mentioned above, and it would be better to prepare this salt beforehand. It can be made by simply dissolving two hundred and fifty grams of a crystallized salt of copper in fifteen hundred grams of water and adding five hundred grams of pyroligneous acid. These quantities of salt of copper and of pyroligneous acid are sufficient for each kilo of dry extract of logwood. The most advantageous salt of copper for getting a fine tint is nitrate, but it must be very neutral, not impregnated with nitric acid. The sulphate of copper is sufficient in the greater number of cases. A logwood bath, which does not at least contain ten grams of dry extract per liter is too weak to sufficiently nourish the cotton. The first logwood bath ought to have, with the water with which it is diluted, at least fifteen to twenty times the weight of the fabrics.

The work.—When the dry extract of logwood is well dissolved in the necessary quantity of water to make a sufficiently concentrated bath, the fabrics, skeins, &c., will first be submerged in the bath, then moved about in it for three quarters of an hour to one hour, according to the nature of the fabric, the bath being slightly heated the while. The temperatue may be 70°, to 80° centigrade. When carried above that point, good effects are not produced, especially upon cotton. This first immersion in the logwood alone has for its object to thoroughly impregnate, penetrate, and tan the threads. After the space of time above mentioned, the copper solution, prepared beforehand, will be added. But this addition may be made all at once or in two or three times, according to the resistance to the dye, resistance which the different fabrics and threads are known to have. If the fabric is very easy to dye, the copper solution will be added all at once; if it is more difficult, it will be added in two parts; lastly, if it is very difficult, it will be added in three parts. If the copper solution is added all at once, the fabric must be moved in the bath during the space of three-quarters of an hour to one hour; if the solution is added in two parts, the fabric must be moved during one-half hour each time; lastly, if one third of the solution is added at a time, the moving must be continued during twenty-five minutes at least for the first third of solution, thirty-five minutes for the second third, and forty-five minutes for the last third. During the whole of the time the copper solution is in the bath, the temperature will be kept the same as for the logwood alone, that is to say from 70° to 80° centigrade; it may even be carried to 90° during the last quarter of an hour. The total quantity of copper liquid must be such that it brings to the bath a quantity of sulphate of copper or neutral nitrate of copper, which amounts to one-quarter at least of the quantity of dry extract of logwood, which is in the bath. The quantity of the copper solution may be carried as far as one third of the quantity of logwood extract. If liquid extract of logwood is used (30° Baumé), one hundred and fifty to two hundred grams of sulphate of copper or of nitrate will be necessary for each

kilogram of extract. The manner in which the copper solution has been prepared beforehand, will show what quantity in weight or by measure will correspond to one, ten, or one hundred parts of logwood. After these first phases of the dyeing in the logwood alone, then in the logwood and the copper liquid, the fabrics, threads, &c., are taken out of the bath, then left to drip, and lastly to dry in the air a little. The bath is kept for use in other operations, by putting in each time sufficient logwood and copper solution for the next fabrics or skeins to be dyed, and not in proportion to the volume of the bath as at the outset.

Fixing.—In order to fix the logwood and copper given to the fabrics, threads, &c., by the first bath, they are passed into the second bath, which will be composed of water only, to which has been added the fixing-mixture prepared beforehand. For one hundred kilos of fabrics, for instance, it will be necessary to prepare a bath composed of thirteen hundred liters of water at least, into which will be poured one hundred liters of one of the fixing mixtures given above. The fabrics, skeins, &c., from the first bath will be submerged therein. Care must be taken to see that this second bath is still slightly alkaline when the fabrics are put in. Should this not be the case, on account of the small quantity of pyroligneous acid brought away from the first bath, a little carbonate of soda or ammonia will be added, and then the fabrics will be moved in the bath during fifty to fifty-five minutes and even during one hour to one hour and a quarter. The bath will be heated to the same temperatures as the first one, and even nearly up to 100° centigrade. The fixing operation will take more or less time, according to the quantity of cotton in the fabrics or skeins and the position which the cotton occupies in them. For pure cotton fabric or skeins, fifty to sixty minutes will be sufficient, but for pure wool, two hours will be necessary. For mixed fabrics, in which the cotton can be seen, the time of fixing will be one hour to one hour and a quarter. For mixed fabrics, in which the wool is outside, one hour to one hour and a half is not too long. Care must be taken not to make the rollers, which guide the fabrics into the baths, turn too fast, for cotton especially gets dyed much better when the movement is a slow one. A quick movement is favorable for washing only.

The fabrics, skeins, &c., taken out of the second bath need only be rinsed and dried in the air.

After the fixing bath has been once used it is thrown away.

Instead of dyeing in two separate baths, my method may be used with one bath only. In that case, all that has to be done is to put into the first bath the composition which is used as a fixing mixture, and that at the moment when the work done by the logwood and copper solution is thought to be sufficiently advanced, the first bath, after the fixing mixture has been added, will act in the same way as the second one. The only care to be taken is to add any alkali in a small quantity, to make sure of the slight alkalinity of the fixing mixture. But, when only one bath is used, it will be necessary to increase the quantity of the fixing mixture by twenty per cent. at least, and also to give a little more time for the fixing process. Then the bath can only be used once, for, having received the fixing mixture, it cannot again have logwood put into it. If then, it happens that it is preferable to do the dyeing in one bath, the introduction of the fixing mixture in two parts will offer some advantages. The said mixture will then be divided into two parts, and when one part has been put in, sufficient time will be left before the introduction of the second part.

Remark.—Of course I may add, to the logwood used in this method, more or less yellow wood, cuscuma, quercitron, sumac, &c., all of which, chosen among the tannins, are capable of modifying the black color. I may also add certain colors derived from tar, and other sources, and the coloring properties of which may of course, co-exist with those of logwood, and resist the action of the fixing mixture.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is—

1. The process of dyeing in black, consisting of first submitting the goods to be dyed to a bath composed of water, logwood and a copper salt; then immersing the goods in a second fixing bath composed of water, metallic sulphates, bi-chromate of potash and neutralized nitrated starch, the solution being rendered slightly alkaline by the addition of soda potash or ammonia, substantially as herein described.

2. In a process of dyeing in black, a second or fixing bath composed of neutralized nitrated starch, alum, metallic sulphates, bi-chromate of potash and a small quantity of soda or ammonia, substantially as described.

In witness whereof I have hereunto set my hand in presence of two witnesses.

CHARLES FRANÇOIS XAVIER NOROY.

Witnesses:
PAUL RUBY,
ALEXANDRE HUBANT.