UNITED STATES PATENT OFFICE.

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PROCESS OF VAT-DYEING WITH GALLOCYANIN DYESTUFFS.

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To all whom it may concern:

Be it known that we, JOSEPH BIERER, chemist, a citizen of the French Republic, and HERMAN LORÉTAN, chemist, a citizen of the Swiss Republic, residents of Basel, Switzerland, have invented a new Process of Vat-Dyeing with Gallocyanin Dyestuffs.

Hitherto dyeing with the various coloring matters of the gallocyanin series and with derivatives thereof has been accomplished by boiling, this being more especially done in dyeing fibers, or fabrics, which have been previously mordanted or which have been mordanted and discharged. We have ascertained that this dyeing can be satisfactorily accomplished at low temperatures, or in the cold, and on all fibers and fabrics, whether mordanted, or not, by starting from the leucoderivatives of gallocyanin dyestuffs. It is more advantageous to effect the dyeing with mordanted fibers, or fabrics, the richness and the fastness of the dyeings being of a superior nature, and the process more expeditious but mordanting is not a necessity. As mordants we start either from the tannin mordants, either in the pure state, or as extracts (such as extracts from sumac, logwood, reduced or not, oak-wood extracts etc.), or from metallic mordants preferably alumina and iron mordants, although other mordants such as those of chromium, may be used or metallic mordants combined with tannin mordants, or mixtures of metallic mordants may be used.

The process is to be carried out with a leucogallocyanin in a vat having a slightly acid reaction, it being kept in a reducing state by small addition of hydrosulfite. The preparation of the vat is very simple and its concentration may be varied to any required extent.

If a vat containing 100 liters of water in which are dissolved for instance 100 to 500 grams of the leucoderivative of a gallocyanin dyestuff, then 50 to 100 grams of concentrated hydrosulfite N F, or any other hydrosulfite should be added, but the hydrosulfite should not be alkaline enough to destroy the acidity of the vat. The vat thus prepared assumes a yellowish to yellow-brownish color, and is very limpid. If this coloration be not obtained, more hydrosulfite should be added. Hard water should not be used without previously softening it. As already stated the vat should be slightly acid and if this be found not to be the case, a small quantity of a mineral acid (hydrochloric acid for instance) or of formic acid, say 10 grams per 100 liters, should be added. According to circumstances this quantity may be increased. Instead of dissolving the leucoderivative of the gallocyanin dyestuff directly in the vat, it is possible to start from an unreduced gallocyanin dyestuff and to effect the reduction in the vat itself, and obtain the same result, but the direct use of the leucoderivative is preferable and simpler. The acidity of the vat has for its object to avoid the oxidation of the coloring matter in the vat itself and its precipitation. The mordanting of the fabrics, or fibers, can be effected in any known, or suitable manner.

For dyeing, the goods are passed through the aforesaid reduced vat at a low temperature, varying from 25° to 50° centigrade for from 1 to 3 minutes, according to the depth of color required. On leaving the vat the goods are squeezed and then, in the case of mordanted fabrics, to make the shades uniform and economize and maintain the oxidizing bath, the goods are then washed either in running water, or by any other suitable means, washing in cold water having no effect on the result of the dyeing, the firm fixation of the coloring matter in the cold being a particular feature of the process according to this invention. After washing (which is optional) oxidizing is effected in the cold by passing the goods rapidly through an oxidizing bath containing from 2 to 5 grams of sodium bichromate or of another bichromate, per liter, this operation having for its object to completely develop and fix the coloring matter, for this operation serves not only to develop, but also to fix, the dye. According to the shades desired, other metallic salts may be added to the bichromate, such as a salt of iron, or copper sulfate or the like, either for greening, tarnishing, or deepening or otherwise affecting the shades, these additions in some cases, greatly increasing the fastness of the dyes. The goods are then washed, soaped and dried.

The process of dyeing according to this invention is not only applicable to fabrics, plaits and stocking-net and the like, but also

to fibers, or threads, in skeins, or on spools, or cops, and to textile fibers or flocks, and may in these cases be efficiently carried out in the apparatus used for the ordinary dyeing of such goods, the order of operations hereinbefore described being followed. The said process is applicable to cotton, wool, or silk, and to all vegetable, animal or artificial fibers, or fabrics, or filaments generally such as hair, artificial silk, flax and the like, and also to paper and leather and like substances. The shades obtained are very uniform and satisfactory and fast and vary from bright shades to dull shades according to the mordant, or mordants, and developer, or developers, used. Alumina or tannin, used alone or in combination as mordant and bichromate used as the oxidizing agent, gives shades of great vividness, but iron, on the contrary, used either by itself or with tannin as mordant and bichromate with copper and iron used as the oxidizing bath, gives the darkest shades, almost a black color, while other mordants give intermediate shades. For the colored or white discharged articles, alumina or tannin mordants are preferably used either alone, or together, as these mordants enable discharge to be obtained giving a clean and pure white, and also bright colored discharge effects. The other mordants although they may be used for this purpose are not generally so advantageous. It will suffice to print with oxidizing discharge known as "chlorate-prussiate" and to steam according to the usual method.

As apparatus suitable for carrying out the process according to this invention are of a varied nature, and of a well known kind, no special apparatus need be described.

By the direct addition of the mordants to the vat, the shades may be varied; for instance the addition of tannin gives a bluer shade, but such addition to the vat is not however to be recommended if it can be avoided, because it tends to cause precipitation in the vat, which is injurious to efficiency and to uniformity of the dyeings. The best way is to apply the mordants to the goods beforehand.

The vats can of course, like indigo vats, be used over and over again if they be supplied with coloring matter and other ingredients, as required.

The following are examples of how this invention can be performed, but the invention is not limited to these examples:

Example I: A vat is prepared with 100 liters of water at 40° centigrade, 0.500 kilogram of the leucoderivative of the gallocyanin resulting from the condensation of nitrosodimethylanilin with gallamic acid (in powder) dissolved in 10 liters of water, 0.500 kilogram of pure sodium formaldehyde sulfoxylate and 0.050 kilogram of hydrochloric acid of 20° Bé. The vat thus prepared soon assumes a yellowish color and is suitable for dyeing *in vacuo* dark shades on fibers, threads, or filaments on spools, or cops, without boiling. The vat liquid is, by suction, caused to circulate through the goods, which may be done by any known, or suitable method, and then suction is increased to remove excess of liquid. The bichromate bath containing from 5 to 10 grams of bichromate per liter is then caused to circulate in a similar manner at a temperature of about 40° centigrade through the goods. The dye is thus completely developed, the goods are then washed, and will be found to be dyed throughout very uniformly. The shade obtained is violet blue.

Example II: A vat is prepared with 100 liters of water, 100 grams of the leucoderivative of the gallocyanin resulting from the condensation of nitrosodimethylanilin with gallamic acid (in powder) 25 grams of concentrated N F hydrosulfite and 5 grams of hydrochloric acid of 20° Baumé. As soon as the vat has assumed a yellowish appearance, goods previously mordanted in the usual way with tannin, and tartar-emetic, are dyed cold by means of the "jigger". According to the depth of shade required, the passes are repeated several times after the vat has been resupplied with the dyeing ingredients. The fabric is washed in cold water, and then passed through the oxidizing bath and washed, soaped and dried. The shade obtained is a rich blue-violet which is very uniform and fast. This shade on tannin is easily discharged by the oxidizing discharge, the so-called chlorate-prussiate, whereby fine white grounds are obtained this differentiating this process from the usual process of dyeing on tannin by basic coloring matters wherein the discharge is usually effected by caustic soda, before dyeing.

Example III: In a vat prepared with 1 gram of chromacetin blue S (a mixture of leucoderivatives of gallocyanin dyestuffs) per liter, with the other materials and proportions the same as in Example II, the dyeing is effected by dipping for three minutes in the cold, the goods mordanted with alumina. The goods are washed in the cold, passed through the bichromate bath, washed, soaped and dried. The shade obtained is a dark blue, a kind of average indigo blue, perfectly adapted to the production of discharge effects by the above specified oxidizing discharger.

Example IV: In a vat prepared as aforesaid with 10 grams of phenocyanin in the state of paste per liter, goods mordanted, according to the known methods, with alumina and tannin is dyed in the cold by dipping it for three minutes in the vat. The goods are slightly washed in cold water, passed through bichromate, washed, and

dried. The shade obtained is a pure blue which is very vivid and can be perfectly discharged.

Example V: Through a vat prepared as in Example II, but raised to a temperature of 50° centigrade, goods mordanted with alumina are passed, then washed in cold water, passed through a bichromate bath containing 2 grams of bichromate per liter and 2 grams of copper sulfate. Wash and finish as above stated. The shade is darker and faster than would be the case if a bichromate bath alone had been used.

Example VI: The operations are, as stated in Example V, but the oxidizing bath has added to it 10 cubic centimeters of iron acetate of 12° Baumé for each liter of the bath. The shade is darker than in Example V without loss of any of its qualities of fastness.

Example VII: Into a vat prepared as explained with 1 gram of the leucoderivative of the gallocyanin resulting from the condensation of nitrosodimethylanilin with gallamic acid (powder) per liter, or any other leucogallocyanin such as the modern blues, modern cyanins and the like, goods mordanted with iron and alumina are dipped for 3 minutes at a temperature of 30° centigrade. They are then washed, passed through bichromate and finished as hereinbefore explained. The shades obtained vary from purple-blue to greenish-blue and are of excellent fastness. On fabrics mordanted with iron only, blue-blacks are obtained with reddish or greenish sheen.

Example VIII: By a previous mordanting of the goods with a compound mordant either of reduced logwood and aluminium acetate, or of reduced logwood, Persian grain, or yellow berries, and aluminium acetate in accordance with the various known methods and by passing the goods as hereinbefore described through a vat prepared with any kind of leucogallocyanin, very dark blues are obtained varying from a greenish to a reddish shade. These are fast and economical and can be easily discharged and enable all the indigo shades to be imitated.

Example IX: By padding the goods in a bath of 80 grams of solid extract from Persian grain, or yellow berries, or of any other yellow extract, 10 grams of acetic acid and 910 grams of aluminium acetate of 5° Baumé, by drying in a "hot flue", steaming 5 minutes in a Mather & Platt apparatus at 100° centigrade, passing through a chalk bath, and washing, a yellow ground is obtained which, on being passed for instance through a phenocyanin vat, prepared as hereinbefore described, gives a fine vivid green. In a vat prepared with modern cyanins fast olive shades which can be discharged are obtained.

The hereinbefore described dyeing operations can also, as in the case of indigo, be done on goods already dyed with other direct basic, sulfureted, and like coloring matters, their performance being in this case the same as on white goods, by mordanting or not.

What we claim is:

1. The described process for dyeing gallocyanin dyestuffs on vegetable, animal or artificial substance, consisting in treating the said substance at a temperature lower than 50° C. in a slightly acid vat prepared so as to contain a leucoderivative of a gallocyanin dyestuff and a small quantity of a reducing agent for preserving the vat and then developing and fixing the dyestuff thus applied to the said substance by its oxidation on the same.

2. The described process for dyeing gallocyanin dyestuffs on vegetable, animal or artificial substance, consisting in mordanting the said substance, then treating it at a temperature lower than 50° C. in a slightly acid vat prepared so as to contain a leucoderivative of a gallocyanin dyestuff and a small quantity of a reducing agent for preserving the vat and finally developing and fixing the dyestuff thus applied to the said substance by its oxidation on the same.

3. The described process for dyeing gallocyanin dyestuffs on vegetable, animal or artificial substance, consisting in treating the said substance at a temperature lower than 50° C. in a slightly acid vat prepared so as to contain a leucoderivative of a gallocyanin dyestuff and a small quantity of a reducing agent for preserving the vat and then developing and fixing the dyestuff thus applied to the said substance by passing it through an oxidizing bath.

4. The described process for dyeing gallocyanin dyestuffs on vegetable, animal or artificial substance, consisting in mordanting the said substance, then treating it at a temperature lower than 50° C. in a slightly acid vat prepared so as to contain a leucoderivative of a gallocyanin dyestuff and a small quantity of a reducing agent for preserving the vat and finally developing and fixing the dyestuff thus applied to the said substance by passing it through an oxidizing bath.

5. The described process for dyeing gallocyanin dyestuffs on vegetable, animal or artificial substance, consisting in treating the said substance at a temperature lower than 50° C. in a slightly acid vat prepared so as to contain a leucoderivative of a gallocyanin dyestuff and a small quantity of a reducing agent for preserving the vat and then developing and fixing the dyestuff thus applied to the said substance by passing it through an oxidizing bath containing a metallic salt for modifying the dyeing.

6. The described process for dyeing gallocyanin dyestuffs on vegetable, animal or artificial substance, consisting in mordanting the said substance, then treating it at a temperature lower than 50° C. in a slightly acid vat prepared so as to contain a leucoderivative of a gallocyanin dyestuff and a small quantity of a reducing agent for preserving the vat and finally developing and fixing the dyestuff thus applied to the said substance by passing it through an oxidizing bath containing a metallic salt for modifying the dyeing.

In witness whereof we have hereunto signed our names this 14th day of May, 1907, in the presence of two subscribing witnesses.

JOSEPH BIERER.
HERMAN LORÉTAN.

Witnesses:
GEO. GIFFORD,
AMAND RITTER.