UNITED STATES PATENT OFFICE.

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PROCESS OF DYEING INDIGO.

SPECIFICATION forming part of Letters Patent No. 710,800, dated October 7, 1902.

Application filed May 19, 1900. Serial No. 17,278. (Specimens.)

To all whom it may concern:

Be it known that I, FRITZ PETERHAUSER, chemist, a citizen of Switzerland, residing in Höchst-on-the-Main, Germany, have invented new and useful Improvements in Indigo-Vat Dyeing, of which the following is a specification.

The dyeing of textile fabrics in the indigo-vat differs from dyeing with other natural or artificial dyestuffs principally by the fact that hitherto it has been impossible to produce deep shades of indigo by one immersion in a single dyeing operation. This fact results from the indigo-white having in the ordinary vats only a limited affinity for the animal or vegetable fiber, so that when merely one immersion is given only a small portion of the indigo contained in the vat fixes on the fiber as indigo-white, and consequently only a certain intensity of color is obtained. In a very concentrated vat, however, it is possible to obtain deep colors; but then they are not fast to washing and rub off easily, being, so to speak, "fixed superficially." The only way to obtain deep colors on the animal or vegetable fiber fast to washing and not liable to rubbing off consisted hitherto in repeated dyeing operations in order to sufficiently fix the indigo on the fiber—namely, by several immersions. This method, however, requires much time and labor, and consequently is very expensive.

I have succeeded in rendering dyeing by repeated immersions unnecessary and have found a process of producing on the fiber by one immersion colors of deeper intensity than any hitherto obtained, which are fast to washing and do not come off when rubbed.

I have found that the affinity of free indigo-white for animal and vegetable fiber is much greater than that of the indigo sodium or lime salt hitherto employed in the vats. It was impossible with the present knowledge of indigo dyeing to obtain dyes in a vat containing free indigo-white—that is to say, in a neutral or even acid vat—for free indigo-white behaves like an acid which requires an excess of alkali to dissolve it, and from its solution feeble acids (even carbonic acid) precipitate it. In this separated form it has no affinity for the fiber. I have found that the separation of indigo-white in a neutral or even acid bath can be avoided by an addition of certain substances—such as gum, glue, gelatin, dextrin, starch, and the like—and I obtain by a single immersion in vats thus prepared dyes which do not rub off and are of an intensity of color such as hitherto could only be obtained by several immersions.

The nature of this invention therefore consists in adding to the vat prepared in the usual manner a substance having the property of keeping the indigo-white dissolved in a neutral or acid liquid, it thus being no longer necessary throughout the process to keep the vat alkaline, a neutral or even acid reaction being produced during the immersion of the goods by a gradual addition of acids or acid salts. The alkali may also be neutralized immediately before introducing the goods instead of during the dyeing process. A dilute solution of sodium bisulfite or an aqueous solution of sulfurous acid is best suited for acidifying the vat; but other acid salts or acids——such as lactic, hydrochloric, or acetic acid—may also be used, which, together with the salts in the vat, do not produce any insoluble precipitates. The best results in practice are obtained with the hydrosulfite vat, while those having a sediment—such, for instance, as the zinc-dust-lime and sulfate-of-iron-lime vat—are less suited for this dyeing process, as the sediment appears to combine mechanically with the greater portion of the substance added for dissolving the indigo-white; but if the clear vat liquid is drawn off from the sediment then the last-named vats yield also good results. This process is suited for animal and vegetable fibers for the dyeing of pieces, yarns, or loose material and ought to be of great value for dyeing with apparatus. While almost completely exhausting the bath by one immersion, indigo-vat dyes are obtained of an intensity of color such as could only be obtained hitherto by several immersions. The dyeing is thorough and the fastness to milling and rubbing far superior as compared with the equally deep dyes obtained in the

ordinary manner. Besides, the solidity of the fiber, its brilliancy, its fitness for being spun, especially when the material is wool, are much increased by the reduction of work in a vat which is not alkaline and are much greater than in the case of fiber dyed in ordinary indigo-vats.

This process differs essentially from that described in the German Patent No. 58,124, by which a uniform "turning green" of the dyed fabrics is obtained and which covers (p. 2 1.2) "the preparation of a weak alkaline hydrosulfite vat containing just the quantity of alkali requisite for dissolving the indigo-white." It purposes above all to reduce the two alkaline hydrosulfite vats to their normal strength by repeated operations, whereas I operate with baths of a neutral or even decidedly acid reaction. The present process differs also greatly from that of the German application B 20,772. While in the process which is the subject of the present invention good results are obtained on animal and vegetable fibers by dyeing in neutral or acid vats with the addition of gum, glue, gelatin, and similar substances which tend to keep the free indigo-white in solution till it is combined with the fiber, the application B 20,772 refers only to the dyeing of vegetable fiber in the usual alkaline vats and the addition to the vat of protein substances, or the previous preparation of the fabrics with such substance has only for its object to animalize the vegetable fiber—that is to say, to produce a higher affinity of the indigo-white salt for the vegetable fiber.

The following example illustrates the process, it being understood that the quantity of the substance added to dissolve the indigo-white is to vary according to the nature of the substance and whether the dyeing takes place in a freshly-prepared or an old bath.

Blue on Fifty Kilos of Slubbing Dyed with the Obermayer Machine.

1. *Preparation of the hydrosulfite, (two hundred liters.)*—Twenty-four liters of sodium bisulfite (38° to 40° Baumé specific gravity) are diluted with one hundred and fifty liters of water at a temperature of 20° to 25° centigrade, to which are slowly added, while stirring, four kilos of zinc-dust made into paste with water. The whole is then further stirred for another half hour. Three to four kilos of burnt lime (according to its strength) are slaked with water and stirred with twenty liters of water to form milk of lime, this mixture being added half an hour later to the hydrosulfite solution. The whole is allowed to stand for one hour after the last addition, and the clear solution is then drawn off.

2. *Preparation of the original vat.*—Five kilos of pure ground indigo (one-hundred-percent. strength) and six liters of soda-lye of 40° Baumé specific gravity (that is to say, the smallest quantity of alkali requisite to convert the indigo employed into indigo-white sodium salt) are diluted with ten liters of water, to which are added one hundred and eighty liters of the above-described hydrosulfite solution. The whole is heated to 60° centigrade till all the indigo is dissolved and reduced.

3. *Dyeing.*—The apparatus is prepared with fifty kilos of well-wetted slubbing, to which is added the requisite quantity of water, (according to the size of apparatus), and the whole is heated to 50° centigrade. Then forty liters of the original vat (containing one kilo of indigo) are introduced, and the apparatus is started. Then five liters of ten-per-cent. glue solution are added, and, by means of a dripping apparatus, six and one-half liters of sodium bisulfite of 40° Baumé specific gravity diluted with water till the vat assumes an acid character. At the expiration of a quarter of an hour the vat is nearly exhausted. The slubbing is taken out and oxidized in the usual manner.

Having now described my invention, what I claim is—

The herein-described improvement in indigo-vat dyeing, which consists in first adding to the hydrosulfite vat protein substances as herein described, and then neutralizing the vat with acid bodies, substantially as set forth.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

FRITZ PETERHAUSER.

Witnesses:

ALFRED BRISBOIS,

JOHANN HARTENSTEIN.