

UNITED STATES PATENT OFFICE.

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HYDROSULFITE INDIGO-VAT.

SPECIFICATION forming part of Letters Patent No. 794,050, dated July 4, 1905.

Application filed September 26, 1903. Serial No. 124,972.

To all whom it may concern:

Be it known that I, PAUL SELLET, a subject of the German Emperor, residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria, Empire of Germany, have invented new and useful Improvements in Hydrosulfite Indigo-Vats, of which the following is a specification.

When dyeing wool with indigo from a hydrosulfite-vat, it has hitherto been necessary in practice to employ fixed alkali, such as caustic soda or calcium hydroxid, for the preparation of such vat. The said caustic alkali serves to dissolve the indigo-white formed, and great care and strict attention to details is necessary to obtain good results, since too great a proportion of fixed alkali attacks the wool fiber, and the quality of the dyeings produced may suffer thereby. The preparation of a vat by means of ammonia alone (which does not attack wool) is not possible in practice, because ammonia does not sufficiently dissolve indigo-white.

Various proposals have been made for avoiding or diminishing the disadvantages which the presence of too large an excess of fixed alkali in the vat occasions, and, among others, the addition of ammonium chlorid to the vat has been recommended, the chlorin of this salt combining with the excess of fixed alkaline base and ammonia being set free. This process, however, has several defects. For instance, such dyeings, especially if the shades be deep, are liable to rub off, and the addition of a small excess of ammonium chlorid beyond the amount necessary to transform the free fixed alkali present (that is, the fixed alkali in excess of that which is necessary for effecting the solution of the indigo-white) causes a precipitation of indigo-white in crystalline form, (a fact not generally known,) and the precipitated indigo-white sinks in the vat and becomes unavailable for dyeing, so that this method has not come into general use.

The object of my present invention is to prepare a new hydrosulfite-vat containing no free fixed alkali, but which while alkaline from the presence of ammonia is at the same

time free from the various defects of the aforementioned ammonium-vat. I attain this end by the combined addition to the hydrosulfite-vat of an ammonium salt and a proteid body.

I am aware that proteid bodies have for themselves been added to indigo-vats used for dyeing vegetable fiber, such as cotton, and, as aforesaid, that ammonium salts have for themselves been added to the hydrosulfite-vat for wool-dyeing; but I wish to state distinctly that in this specification I in no way attempt to claim the use in the indigo-vat of either of these bodies used separately, but only when used in combination. By this combination I obtain results which were quite impossible and unforeseen before my present invention. According to it I can produce a vat which while free from fixed alkali, but containing ammonia, produces with few dips dark shades on wool of great evenness and fastness against fulling and rubbing. Owing to the absence of fixed alkali, the wool remains soft and adapted for spinning, since the risk of the fiber being attacked is completely done away with.

Although the alkalinity of my new vat is due to ammonia, (which, as aforesaid, only dissolves indigo-white to a comparatively small extent,) the addition of the proteid body and ammonium chlorid in the preparation thereof either causes no precipitation of indigo-white or causes it to separate in a state of suspension exceedingly favorable for dyeing purposes, and loss of indigo-white or irregular dyeing action thereof from the accidental addition of too much ammonium salt to the vat does not take place. Further, considerably less care and attention to details are necessary than when using the old form of alkaline hydrosulfite-vat, which, added to the possibility of obtaining deep dyeings with few dips, effects a great saving of time and labor.

To show the valuable effect obtainable according to my invention and in order to characterize my new indigo-vat, I cite the following four dyeing experiments. The quantity of indigo-vat and wool employed was in all

cases the same and the dyed pieces of wool were washed and dried under similar conditions. The concentration of the vat was in all cases equal to one (1) gram of indigo per liter; temperature of vat in all cases fifty degrees centigrade, (50° C.); duration of dyeing in all cases twenty (20) minutes. The indigo taken up by the wool was determined by the method Scheurer Brylinsky.

10	Wool dyed in hydrosulfite-vat with addition of—	Percentage of indigo fixed on the fiber.	Percentage increase of indigo fixed on fiber with reference to experiment 1.
15	1. (No addition).....	1.333	
	2. Glue alone.....	1.498	0.182
	3. Ammonium chlorid alone.....	2.528	1.333
20	4. Glue and ammonium chlorid according to present invention.....	4.031	2.725

My new vat is therefore distinguished from all other alkaline-vats hitherto prepared by the property of causing wool to fix on the fiber in one dip and under the conditions mentioned over four (4) per cent. of indigo.

As instances of proteid bodies suitable for the purposes of this invention I specially mention the various kinds of gelatin and gelatinous bodies, such as glue and the like; but of course I do not confine myself to the use of these particular bodies. Any form of hydrosulfite-vat suitable for wool can be employed, and a hydrosulfite solution suitable for the preparation of such vat is conveniently made by dissolving ten (10) kilograms of solid hydrosulfite B. A. S. F. in fifty (50) liters of water to which three-quarters ($\frac{3}{4}$) of a liter of caustic-soda lye containing about thirty-eight (38) per cent. of NaOH has previously been added, stirring until dissolved and preserving in glass or like bottles or vessels from which air is excluded as far as possible. This solution is referred to in the following examples as "hydrosulfite conc. B. A. S. F.", and these examples will serve to further illustrate the nature of this invention, which is, however, not confined to these examples nor to the conditions described therein.

Example 1—Dyeing loose wool.—Prepare a stock vat by mixing five (5) kilos of indigo pure twenty (20) per cent. B. A. S. F.—equal to one (1) kilo indigo one hundred (100) per cent.—two and one-quarter ($2\frac{1}{4}$) liters of caustic-soda lye containing about eighteen (18) per cent. of NaOH, fifteen (15) liters of hydrosulfite conc. B. A. S. F., and warming the whole to fifty degrees centigrade (50° C.) and allowing it to stand for half ($\frac{1}{2}$) an hour. Add this stock vat to a dyeing-vat containing one thousand (1,000) liters of liquid which has previously been sharpened with four hundred (400) cubic centimeters of hydrosulfite conc. B. A. S. F., and then add three and one-half (3½) liters of a ten (10) per cent. solution of

glue. Immerse the wool in this vat, work it about for five (5) minutes, and then within a space of ten (10) minutes allow a solution of six hundred (600) grams of ammonium chlorid in four (4) liters of water to flow into the vat, which is to be kept stirred. After having added the ammonium chlorid keep the wool in the bath for five (5) minutes, then squeeze it between rollers and allow it to oxidize. The total length of time required for the operation is usually almost twenty (20) minutes, and the temperature is from about fifty (50) to fifty-two (52) degrees centigrade.

Example 2—Dyeing woolen yarn.—Prepare a stock vat by dissolving six and two-thirds (6⅔) kilos of indigo-white paste, fifteen (15) per cent. B. A. S. F.—equal to one (1) kilo indigo one hundred (100) per cent.—in one and one-tenth ($1\frac{1}{10}$) of a liter of caustic-soda lye containing eighteen and a half (18½) per cent. of NaOH and adding thereto four (4) liters of hydrosulfite conc. B. A. S. F. and six (6) liters of boiling water. When the indigo-white is completely dissolved, add this stock vat to a dyeing-vat containing one thousand (1,000) liters of liquid which has previously been sharpened with four hundred (400) cubic centimeters of hydrosulfite conc. B. A. S. F., and then add three and a half (3½) liters of a ten (10) per cent. solution of glue. Immerse the wool as in Example 1 and add a solution of one-quarter ($\frac{1}{4}$) of a kilo of ammonium chlorid in three (3) liters of water under the same conditions as explained in Example 1 and work the wool for a further five (5) to ten (10) minutes and then wring it out and oxidize. Since this indigo-white vat requires proportionately less caustic soda for setting it than does the indigo-vat of Example 1, the quantity of ammonium chlorid employed is smaller than in that example.

Example 3—Dyeing shabbing.—Prepare a stock vat by warming together at a temperature of fifty degrees centigrade (50° C.) seven and a half (7½) kilos of indigo pure twenty (20) per cent. B. A. S. F.—equal to one and a half (1½) kilos of indigo one hundred (100) per cent.—three and four-tenths ($3\frac{4}{10}$) liters of caustic-soda lye containing about eighteen and a half (18½) per cent. of NaOH and twenty (20) liters of hydrosulfite conc. B. A. S. F. and allow the whole to stand for half ($\frac{1}{2}$) an hour. Add this stock vat to a suitable dyeing-vat containing one thousand (1,000) liters of liquid previously sharpened with half ($\frac{1}{2}$) a liter of hydrosulfite conc. B. A. S. F. Then add three and a half (3½) liters of a ten (10) per cent. solution of glue and a solution of one (1) kilo ammonium chlorid dissolved in five (5) liters of water, as described in Example 1, the dyeing also being conducted as described in that example. The amount of ammonium chlorid added is increased to correspond with the larger quantity of caustic-soda lye employed.

The further feeding of the vats is effected by means of the hereinbefore-described stock vats with the addition of first a half ($\frac{1}{2}$) and then a third ($\frac{1}{3}$) of the quantities of the glue solution
5 stated in the examples and so much ammonium chlorid or other ammonium salt is added as corresponds to the quantity of free alkali present in the stock vats. Should a vat after protracted working become green, it
10 should be sharpened up by the addition of from one-half ($\frac{1}{2}$) liter to two (2) liters of hydrosulfite conc. B. A. S. F. for every one thousand (1,000) liters of vat liquid.

I claim—

15 A composition of matter adapted to serve as an indigo-vat containing hydrosulfite which,

when of a concentration of one (1) gram of indigo per liter of vat, and at a temperature of fifty degrees centigrade (50° C.) and alkaline with ammonia as described, is capable of
20 causing wool to fix on the fiber about four (4) per cent. of indigo in one dip, the duration of the operation being about twenty (20) minutes.

In testimony whereof I have hereunto set
25 my hand in the presence of two subscribing witnesses.

PAUL SELLET.

Witnesses:

JOHN L. HEINKE,
JACOB ADRIAN.