

UNITED STATES PATENT OFFICE.

ARTHUR GEORGE GREEN, OF HEATON MOOR, AND ALEXANDER MEYENBERG, OF MANCHESTER, ENGLAND, ASSIGNORS TO THE CLAYTON ANILINE COMPANY, LIMITED, OF CLAYTON, MANCHESTER, ENGLAND.

PROCESS OF DYEING THIOSULFATE COLORS.

SPECIFICATION forming part of Letters Patent No. 681,117, dated August 20, 1901.

Application filed February 2, 1901. Serial No. 45,710. (No specimens.)

To all whom it may concern:

Be it known that we, ARTHUR GEORGE GREEN, F. I. C., F. C. S., residing at 13 King's Drive, Heaton Moor, near Stockport, and
5 ALEXANDER MEYENBERG, Ph. D., residing at 13 Nelson street, Ardwick, Manchester, in the county of Lancaster, England, have invented a certain new and Improved Method of Dyeing; and we do hereby declare the fol-
10 lowing to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

Although the coloring-matters of the
15 "vidal" or "sulfid" class have acquired a constantly-increasing importance, especially for black dyeing, their general employment has been greatly retarded by several grave disadvantages. These are (a) a tendency to
20 render the cotton-fiber rotten or "tender," more particularly after the goods have been stored for some time or when undergoing subsequent steaming or hot pressing; (b) a tendency to give uneven or bronzy dyeings in con-
25 sequence of precipitation of insoluble color on the surface of the fiber, necessitating great care to avoid exposure to air during dyeing; (c) necessity for excluding copper pipes, rollers, and the like from the dye-vessels; (d)
30 unpleasant odors arising from the waste liquors when run off.

The sulfid colors are produced by fusion of various organic compounds with sodium sulfid and sulfur and are usually put upon the
35 market in a form containing the coloring-matter mixed with sodium sulfid, polysulfids, and other inorganic sulfur compounds. The dyeing is effected by the agency of the sodium sulfid which they contain or which may
40 be added for the purpose. The rotting or "tendering" of the cotton above referred to has been observed more particularly with the black coloring-matters of this class, (see Dr. Chapuis, *Journal of the Society of Dyers*
45 *and Colourists*, 1900, page 84,) and investigation has led to the conclusion that the destructive effect is due to the deposition of finely-divided sulfur upon the cotton fiber during the process of dyeing, which sulfur
50 subsequently becomes oxidized to sulfuric

or sulfurous acid, which "tenders" or rots the cotton. The sulfur thus deposited must either arise from free sulfur or polysulfids contained in the dyestuff or be produced during the dyeing operation by oxidation of the
55 sulfid of sodium present. The tendering or rotting action, together with the other disadvantages above mentioned, which are also attributable to the presence of sodium sulfid, should therefore be avoidable if the color
60 could be used in a form free from admixture with inorganic sulfur compounds and if the sodium sulfid required for dyeing could be replaced by another reducing agent. The use of glucose and caustic soda has long ago been
65 suggested for this purpose, (see German Patent, No. 113,195, of April 10, 1897;) but attempts made to replace sodium sulfid by this agent have so far proved unsuccessful in
70 practice, probably because the sodium sulfid in the ordinary dyeing process fulfils a double rôle, and in addition to acting as a reducing agent serves also as a solvent for the coloring-matter. When such sulfid colors are
75 freed from sodium sulfid—as, for instance, by precipitation by carbonic acid or air—they are in general insoluble in water, and when brought into solution as leuco compounds by means of glucose and caustic soda they do
80 not give even dyeings, but upon reoxidation are completely precipitated, owing to want of a substance capable of combining with the re-formed coloring-matter and rendering it sol-
85 uble. After much experiment we have solved these problems in the following manner: First, in order to avoid the presence of inorganic sulfur or sulfids in the dye-bath we make use of the particular class of sulfur coloring-matters which are prepared in aqueous solution by means of sodium thiosulfate without the em-
90 ployment of sulfur or sulfids and which, although presenting close relationship with the melt colors, are chemically distinct therefrom. These coloring-matters—as, for exam-
95 ple, Clayton fast black, Clayton fast brown, &c.—are put upon the market in a pure form entirely free from inorganic sulfur compounds. They are insoluble in water, and in order to bring them into solution we heat them with neutral sodium sulfate. With this 100

salt they combine to form easily-soluble stable compounds (probably salts of thiosulfonic acids) which, although themselves possessing no dyeing properties, are readily converted
 5 by reducing agents into dyeing leuco compounds, (probably sulfhydryl derivatives,) sodium sulfite being re-formed. The dyeing takes place as the leuco compound is oxidized by the air, and the sodium sulfite present
 10 plays the further important rôle of combining again with that portion of the re-formed coloring-matter which is not taken up by the fiber, thus holding it in solution for later use and preventing uneven dyeing. For effect-
 15 ing the necessary reduction various reducing agents may be employed; but we have at present obtained the best results by means of glucose and an alkali. These materials we prefer to add to the dye-bath in portions
 20 throughout the dyeing and in quantity sufficient to maintain the color in a satisfactorily-reduced condition.

The following example illustrates the general method of procedure: Six pounds of
 25 "Clayton fast black B. M." or "Clayton fast black B conc" are dissolved, with the addition of six pounds of neutral sodium-sulfite crystals, in about two gallons of boiling water. The solution is added to forty gallons
 30 of boiling water containing three pounds of calcined soda and ten to twenty pounds of salt. The bath thus prepared is used, for instance, for dyeing cotton piece goods on the ordinary jigger in the following manner: The
 35 goods are passed twice through the boiling bath, and then while still running a solution of two pounds of glucose and six pounds of caustic-soda lye, (65° Twaddell,) mixed cold, is added in portions of one-fifth every ten
 40 minutes. The dyeing is complete in about one hour, and the goods are then caused to

pass direct from the dye liquor between squeezing-rollers into another jigger containing warm water for washing. If a high degree of fastness be required, the color is sub-
 45 sequently fixed by passing the goods through a hot solution containing three per cent. of copper sulfate, one per cent. of sodium bichromate, and three per cent. of acetic acid, all calculated on the weight of the cotton. A
 50 perfectly even dyeing throughout the piece is thus obtained, and the cotton retains undiminished its original strength.

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

1. The new and improved process of dyeing, such process consisting in first rendering soluble thiosulfate colors free from sulfids;
 60 polysulfids or free sulfur, then effecting the dyeing by conversion of the coloring-matter, by solution in aqueous neutral sodium sulfite, into its soluble sulfite compound; and reducing the latter in the dye-bath by means of an
 65 alkaline reducing agent.

2. The new and improved process of dyeing, such process consisting in first rendering a thiosulfate color soluble by means of so-
 70 dium sulfite, then effecting the dyeing by conversion of the coloring-matter, by solution in aqueous neutral sodium sulfite, into its soluble sulfite compound and reducing the latter in the dye-bath by means of glucose
 75 and an alkali.

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

ARTHUR GEORGE GREEN.
 ALEXANDER MEYENBERG.

Witnesses:

ERNALD SIMPSON MOSELEY,
 JOHN WILLIAM THOMAS.