## United States Patent Office.

DANIEL EDOUARD HUGUENIN, OF BASLE, SWITZERLAND, ASSIGNOR TO SOCIÉTÉ L. DURAND, HUGUENIN & COMPAGNIE, OF SAME PLACE.

## BLUE DYE.

SPECIFICATION forming part of Letters Patent No. 411,149, dated September 17, 1889.

Application filed October 30, 1888. Serial No. 289,552. (No specimens.) Patented in France October 3, 1888, No. 193,325.

To all whom it may concern:

Be it known that I, Daniel Edouard Hu-Guenin, a citizen of the French Republic, residing at Basle, Switzerland, have invented 5 certain Improvements in Blue Dyes, (for which a patent has been granted in France, numbered 193,325, dated October 3, 1888,) of which the following is a specification.

My invention relates to dyes for dyeing to fabrics or fibers, animal or vegetable, a deep

or dark blue.

The use of natural indigo as a dyeing material has always been materially affected by the high price of this substance, and for a 15 long time many have sought for means to lower the cost of dyeing with indigo; but so far as known they have met with no success. These attempts have consisted in incorporating with the indigo, either on the fiber or in 20 the dye bath, one or more other natural dyes or materials. The difficulty with these compounds has been that whatever may be the apparent result of the chosen compound, and although the goods dyed may look exactly 25 like those dyed with indigo, there always exists some weakness. Sometimes the cost is increased rather than reduced, or the color will change when exposed to the air or to contact with acids, alkalies, or chlorine; or 30 it may be that the dye will rub off on the hands.

After prolonged researches I have discovered a compound which fulfills almost absolutely the requirements of the problem.

In carrying out my invention I mix with the natural indigo in the dye bath the substance known as "indophenyl," (supposed formula  $C_{48}H_{16}N_2O$ .) This compound produces the desired results, as will be hereinafter described.

Indophenol was discovered by Mr. Horace Koechlin, a chemist, of Loerrach, Baden, with the collaboration of Mr. O. Witt, chemist, of Charlottenburg, near Berlin, Prussia, and it has been patented in the United States under the numbers 261,518 and 263,341.

In preparing my compound dye I proceed as follows: I crush, either separately or together, the indigo and indophenol, and form with the mixture a liquid paste. This paste I thin or dilute with a proper quantity of cold

water. To this mixture I add several substances called "reducers," such as metallic zinc, powdered bisulphite of sodium, salt of tin, and caustic soda. In other words, I use 55 or may use the reducing substances generally employed in dyeing, these substances producing their usual results in my dye bath.

The following-named proportions will serve to produce a dye bath suited for either fab- 60 rics or fiber: indophenol, dry, in powder, one kilogram; water, one hundred liters; indigo, ground into paste with water, the paste containing two hundred and fifty grams of indigo per liter of water, ten kilograms; bi- 65 sulphite of sodium at 39° to 40° Baumé, ten liters; salt of tin, (chloride of tin,) two kilograms; metallic zinc, in powder, 2.500 kilograms.

The above solution is stirred for an hour, 70 and I then add to it liquid caustic soda, 38° Baumé, eight liters. The liquid is again stirred, and next day about twice its volume of cold water is added. Then the mixture is again stirred energetically, as an ordinary 75 indigo dye bath is stirred, and then the liquid is left to stand about twenty-four hours, or perhaps a little longer, until the liquid becomes clear. After this the mechanical processes are the same as those usually followed. 80

If the fabrics or materials from the bath are passed through a solution of bichromate of potash containing two and one-half grams of the bichromate per liter of water, the dye or tint gains in intensity about ten or fif- 85 teen per cent.

The advantages of this mixed dye are as follows:

a. A very material economy in the cost of the dye as compared with that of indigo when 90 the latter is employed alone. This economy is shown by the fact that the same depth of shade produced in my bath by three dippings or soakings therein can only be obtained by employing from five to seven soakings in a 95 bath of indigo alone.

b. Solidity of the color and its resistance to the action of the air, to rubbing, and to the action of acids, alkalies, chlorine, and other destroying agents.

c. Ease of application to the dyeing of all kinds of fibers, vegetable or animal, that may

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be dyed with indigo alone, the manipulations

being the same in both cases.

d. As compared with the length of time required for deposition in the indigo bath, 5 and especially when the ferro-calcic solution is employed, it is not necessary when using my bath to wait until it clears, and it can be fed during the operation, which secures an important economy in time and money and

10 permits of dyeing piece by piece.

The characteristic point on which rests most particularly the novelty of my invention is this, that, while employing only the same reducing agents as those used with in-15 digo alone, the indophenol is deoxidized with greater difficulty and is deposited more slowly on the fiber. On the other hand, the shade or tint of the indophenol alone is a coarse violet-blue, without much character, which is 20 degraded to a grayish violet, and which has an uncertain hold on the fiber, for which reason dyers have never dared to recommend it to their customers for dyeing any material whatever. This dye, taken by itself, has no 25 advantages, and has never been utilized up to this time. However, by the association of this dye—indophenol—with natural indigo, as before described, and influenced at the same time by the reducing agents, as specified, it 30 conducts itself in precisely the same manner as indigo, is decolorized freely, and in dyeing is deposited on the fiber in precisely the same manner as indigo. It is also acted on by the air in the same manner and to the same ex-35 tent as the indigo alone, and augments very sensibly the concentration without modifying the appearance in any appreciable degree. This indicates a special action, an intermediate rôle, which corresponds to that 40 filled by the natural indigo.

I would add that the resistance offered by

my dye is greater under the influence of destructive agents, and that dead cottons are better covered by it than by the indigo alone.

A characteristic feature of my dye, which 45 gives it a decided value as compared with all others so far as known, is this, that in operating by "direct" acid discharge or with the alkaline chromates, or otherwise, the fabric dyed with my dye gives exactly the same re- 50 sult as if reacted on fabrics dyed with indigo alone, if care be taken to slightly aug-

ment the proportions of chromate.

One of the characteristics of the dye or imprints of indophenol is that it oxidizes and 55 becomes darker when one submits a piece dyed therewith to a chrome bath. I profit by this to pass the fabrics or fibers cold from my bath through a bath composed of cold water, one hundred liters; bichromate of pot- 60 ash or soda, 2.500 kilograms. This augments about one-tenth, if not more, the concentration or intensity of the shade.

I would observe that the bichromate above referred to may be replaced by any other 65 oxidizing agent, as very weak calcium-hypc-

chlorite solution.

I do not wish to limit myself to any particular proportions of the materials or substances employed in my bath.

Having thus described my invention, I

claim—

A compound dye for dyeing fabrics and fibers, consisting of indigo and indophenol combined, substantially as set forth.

In witness whereof I have hereunto signed my name in the presence of two subscribing witnesses.

DANIEL EDOUARD HUGUENIN. Witnesses:

ARNAUD RITTER, PHILIPPE GÜSS.