To all whom it may concern:

Be it known that we, Oskar Kaltwasser and Max Gaumer, of Berlin, in the Kingdom of Prussia, German Empire, have invented new and useful improvements in the production of indigo-blue sulfur dye; and we do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

It is known that by heat-decomposing the indophenol series with sulfur and alkali sulfid coloring matters of various shades of indigo-blue are obtained. The product is obtained which has but a very slight affinity for the fiber and dyes unmordanted cotton direct may be obtained. (Compare German Patent No. 132,212.) The process indicated in the aforementioned patent consists in heating an indophenol with sulfur and alkali sulfid at first for several hours to about 140° and then raising the temperature for a short time to 160°. According to the directions given in the examples of this patent the sulfur and alkali sulfid are employed in the proportions of one part of sulfur to four parts of crystallized sodium sulfid.

Now we have observed that when subjecting the typical indophenol to the action of sulfur and alkali sulfid in the aforementioned way, a product is obtained which has but a very slight affinity for the fiber and dyes unmordanted cotton weak bluish shades which are neither fast to soaping nor washing. According to our observations this unsatisfactory result is due to the following facts—namely, the high temperature employed, and, moreover, the relative proportions of sulfur and sulfid prescribed in the German Patent No. 132,212 by the inventor. Especially the latter point is of great importance and is in our opinion the reason why sulfureted dyestuffs of technical interest have up to the present not been obtained from the aforementioned indophenol or its nearest homologues. We have discovered that for the preparation of a valuable dyestuff from these indophenols it is absolutely necessary to perform the process with such quantities of sulfur and sulfid of sodium that upon one molecule of sodium sulfid at least four atoms of sulfur are employed. If the quantity of sulfur is reduced to a proportion corresponding to three or two atoms, products of no technical interest are obtained— as, for instance, according to the directions of the German Patent No. 132,212, which prescribes even less than two atoms of sulfur.

When boiling the above-mentioned indophenols in an aqueous solution with such quantities of sulfur and sodium sulfid as according to our aforesaid observations are essential, a coloring-matter of high technical value is obtained which renders it possible to obtain fast indigo-like shades on cotton. The manufacture of our dyestuff is illustrated by the following example: Thirty kilograms of the sodium salt of the indophenol $\text{C}_6\text{H}_4\text{N} \equiv \text{C}_6\text{H}_4\text{O}$ are slowly added at about 80° centigrade to one hundred and eighty liters of an aqueous solution containing one hundred and twenty kilograms of crystallized sodium sulfid and sixty-six kilograms of sulfur. The solution obtained is heated up to boiling in a vessel combined with a reflux condenser and is kept at the boiling temperature for about twenty-four hours. The mass is diluted with water and from the solution obtained the dyestuff is precipitated by the introduction of a current of air. It is then filtered, pressed, and dried. The product thus obtained is a brown-black powder which is insoluble in water. It dissolves in caustic alkalis with a dull bluish in alkaline sulfids with blue, color. In warm concentrated sulfuric acid the dyestuff dissolves with a violet color. It produces on cotton direct dull greenish-blue tints, which by the action of oxidizing agents are transformed into indigo-blue shades of remarkable fastness.

The following alterations may be made in the above example without materially changing the character of the product obtained.
Instead of the typical indophenol its homologues may be employed, which result, for instance, from the conjoint oxidation of para-amidophenol and orthocresol or metacresol or in a similar manner from para-amido-orthocresol or para-amido-meta-cresol or orthochlor-para-amido-phenol and phenol, ortho or meta cresol.

Having now described our invention and in what manner the same is to be performed, what we claim as new is—

1. The process for the production of an indigo-blue sulfur dye by heating the indophenol:

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\text{OH} \quad \text{N} \quad \text{=O}
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in a boiling aqueous solution with sulfur and sulfid of alkali in such proportions that upon one molecule of crystallized sodium sulfid at least four atoms of sulfur are employed.

2. The indigo-blue sulfur dye obtained as hereinbefore described, said dye being insoluble in water, dissolving in caustic alkalles with a dull greenish-blue color, in alkali sulfids with blue color and in warm concentrated sulfuric acid with violet color, producing on unmodified cotton dull greenish-blue tints, which by subsequent treatment with oxidizing agents are transformed into indigo-blue shades of remarkable fastness.

In witness whereof we have hereunto signed our names, this 5th day of May, 1903, in the presence of two subscribing witnesses.

OSKAR KALTWASSER.
MAX GAUMER.

Witnesses:
HENRY HASPER,
WOLDEMAR HAUPT.