UNITED STATES PATENT OFFICE.

EUGEN ANDERWERT, HERMAN FRITZSCHE, AND HEINRICH SCHOBEL, OF BASEL, SWITZERLAND, ASSIGNORS TO SOCIETY OF CHEMICAL INDUSTRY IN BASLE, OF BASEL, SWITZERLAND.

SUBSTANTIVE ORTHOOXYAZO DYESTUFFS AND A PROCESS OF MAKING SAME.

1,265,031. Specification of Letters Patent. Patented May 7, 1918.

No Drawing. Original application filed October 6, 1915, Serial No. 54,403. Divided and this application filed January 24, 1917. Seral No. 144,243.

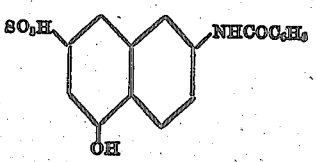
To all whom it may concern:

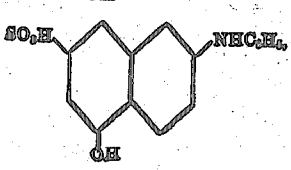
Be it known that we, EUGEN ANDERWERT, HERMAN FRITZSCHE, and HEINRICH SCHOBEL, all three chemists and citizens of the Swiss Republic, and residents of Basel, Switzerland, have invented new Substantive Orthooxyazo Dyestuffs and a Process of Making Same, of which the following is a full, clear, and exact specification.

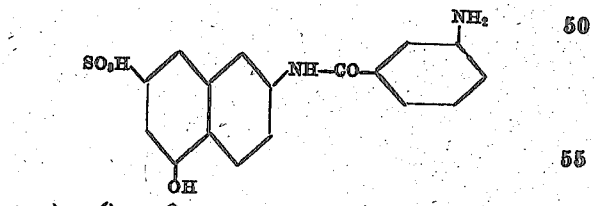
This application is a divisional one of our application for Letters Patent Ser. No. 54403, filed October 6, 1915.

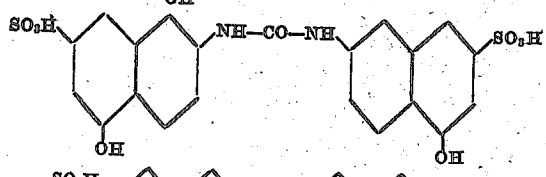
Orthoaminophenol and its derivatives have been employed hitherto exclusively for the manufacture of orthooxyazodyestuffs dyeing mordanted wool, and never for the manufacture of substantive dyestuffs dyeing unmordanted cotton. We have now found that the azodyestuffs containing the diazoderivative of orthoaminophenol or of one of its derivatives and a 2:5:7-aminonaphtholsulfonic or 2:5:1:7-aminonaphtholdisulfonic compound coupled together by the diazoderivative of a primary monoamin having relatively to the amino group a non-substituted position para, as for instance alphanaphthylamin, acid of Cleve, para-cresidin, acetylmetatoluylenediamin and aminophenyloxamic acid, have the properties of substantive azodyestuffs, that is to dye cotton and other fibers without mordant.

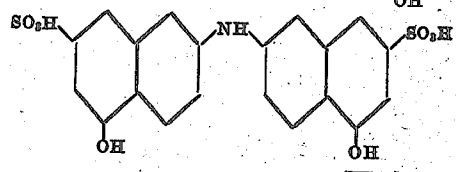
Besides the 2:5:7-aminonaphtholmonosulfonic or 2:5:1:7-aminonaphtholdisulfonic acid one of the following derivatives of 2:5:7-aminonaphtholmonosulfonic acid can be employed:

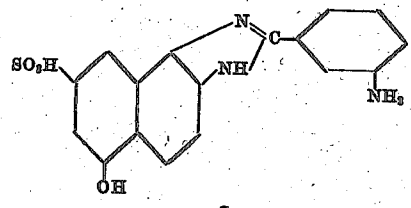


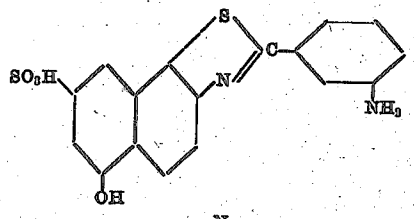


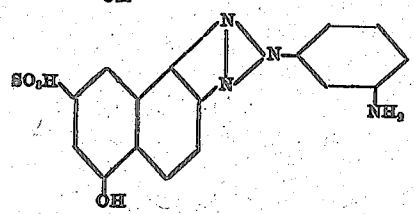


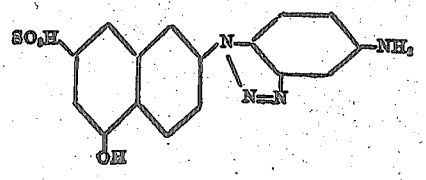


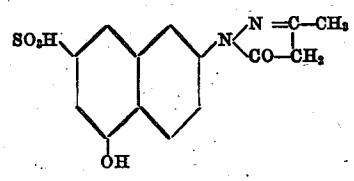












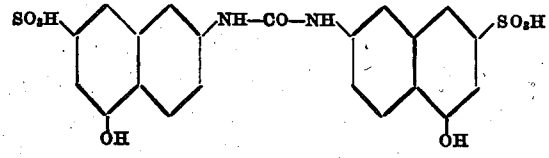
or one of the corresponding derivatives of the 2:5:1:7-aminonaphtholdisulfonic acid.

The new orthooxyazodyestuffs derived in the aforesaid manner from these 2:5:7-aminonaphtholsulfonic or 2:5:1:7-aminonaphtholdisulfonic compounds constitute intense colored powders, yielding with concentrated sulfuric acid deep colored solutions and dissolving in water to solutions changing intensively their coloration on addition of sodium carbonate or of soda lye and dyeing cotton, wool, silk, mixed goods, straw, wood and paper according to the methods used for the known substantive dyestuffs.

The invention is illustrated by the following examples:

Example 1: To the diazoderivative of 18.9 kg. orthoaminophenolsulfonic acid is added the solution of 14.3 kg. alphanaphthylamin in water and 12 kg. hydrochloric acid. The formation of the monoazodyestuff is achieved by stirring at 30–40° C. for a long time. For the purpose of a further diazotizing of the monoazodyestuff, it is transformed, after addition of common salt, into the sodium salt by means of soda lye. To this sodium salt are added at first 7.5 kg. sodium nitrite and afterward quickly 40 kg. hydrochloric acid. After a stirring for 1 hour, the diazo-compound is filtered and poured into a solution of 36 kg. metaaminobenzoyl-2:5:7-aminonaphtholsulfonic acid and of 40 kg. sodium carbonate in water. The dyestuff isolated in the usual way dyes cotton reddish-blue tints and dissolves in water to a bluish-violet solution turning to blue on addition of NaOH.

Example 2: The diazoderivative of 19.9 kg. picramic acid is combined with a solution of 22.3 kg. acid of Cleve and 30 kg. crystallized sodium acetate; the combination is achieved after 24 hours. By transformation into sodium salt, addition of 7.5 kg. sodium nitrite and acidulating with hydrochloric acid the further diazotizing is effected. After a stirring for a long time, the diazocompound is freed from water by suction, transformed again into a paste and poured into a solution of 25.2 kg.



and of 40 kg. sodium carbonate in water. The dyestuff salted out by common salt yields on cotton dull blue tints and dissolves in water to a blue solution turning to a bluish violet on addition of NaOH.

Example 3: 15 kg. 4:2:1-nitroaminophenol are diazotized in the usual manner and the thus obtained diazocompound is added to a solution of 22.3 kg. acid of Cleve and 30 kg. crystallized sodium acetate in water. After stirring for a long time, the combination is achieved by warming to 30–40° C. The monoazodyestuff is after acidulating directly further diazotized with 7.2 kg. sodium nitrite, the resulting diazoazocompound after 2 hours dried by suction, again stirred with water and poured into a solution of 22.3 kg. acid of Cleve and 20 kg. crystallized sodium acetate in water. Before the further diazotation, the thus obtained diazodyestuff is advantageously at first precipitated and separated by filtration and then dissolved again and diazotized again by addition of 40 kg. hydrochloric acid and 7 kg. sodium nitrite. After a stirring of 2 hours the diazoazocompound is poured into a solution of 24 kg. 2:5:7-aminonaphtholsulfonic acid and 40 kg. sodium carbonate in water. The dyestuff isolated in the usual manner yields on cotton green-blue tints and dissolves in water to a blue solution.

Instead of the aminophenol derivatives indicated in the examples, can be employed the corresponding diazoacidylphenol derivatives able to combine more easily, the resulting dyestuffs being saponified after their preparation.

The new dyestuffs are not only suitable for dyeing cotton, wool, silk, leather, straw, wood, paper, mixed goods etc. like the known substantive dyestuffs, but also for the production of lakes and as parent materials for the production of valuable new derivatives.

What we claim is:

1. The described process for the manufacture of new substantive orthooxyazodyestuffs consisting in combining an aromatic orthooxydiazobody with a primary monoamin having relatively to the amino group a non-substituted position para, diazotizing the resulting intermediate product and combining the resulting diazoazocompound with a 2:5:7-aminonaphthosulfonic compound.

2. The described process for the manufacture of new substantive orthooxyazodyestuffs consisting in combining an aromatic orthooxydiazobody with a primary monoamin having relatively to the amino group a non substituted position para, diazotizing the resulting intermediate product and combining the resulting diazoazocompound with a 2:5:1:7 - aminonaphtholdisulfonic compound.

3. The described process for the manufacture of new substantive orthooxyazodyestuffs, consisting in combining an aromatic orthooxydiazobody with a primary mono-

amin having relatively to the amino group a non substituted position para, diazotizing the thus obtained intermediate product, combining the resulting diazoazocompound again with a primary monoamin having relatively to the amino group a non substituted position para, diazotizing the resulting intermediate product and combining the thus obtained diazobody with a 2:5:7-aminonaphtholsulfonic compound.

4. The described process for the manufacture of new substantive orthooxyazodyestuffs consisting in combining an aromatic orthooxydiazobody with a primary monoamin having relatively to the amino group a non substituted position para, diazotizing the thus obtained intermediate product, combining the resulting diazoazocompound again with a primary monoamin having relatively to the amino group a non substituted position para, diazotizing the resulting intermediate product and combining the thus obtained diazobody with a 2:5:1:7-aminonaphtholdisulfonic compound.

5. As new products, the herein described new substantive orthooxyazodyestuffs containing an aromatic orthooxydiazobody and a 2:5:7-aminonaphtholsulfonic compound coupled together by the diazoderivative of a primary monoamin having relatively to the amino group a non substituted position para and constituting intense colored powders, yielding with concentrated sulfuric acid deep colored solutions, dissolving in water to solutions changing intensively their coloration on addition of sodium carbonate or of soda lye and dyeing cotton, wool, silk, mixed goods, straw, wood and paper, according to the methods used for the known substantive dyestuffs.

6. As new products, the herein described new substantive orthooxyazodyestuffs containing an aromatic orthooxydiazobody and a 2:5:1:7-aminonaphtholdisulfonic compound coupled together by the diazoderivative of a primary monoamin having relatively to the amino group a non substituted position para and constituting intense colored powders, yielding with concentrated sulfuric acid deep colored solutions, dissolving in water to solutions changing intensively their coloration on addition of sodium carbonate or of soda lye and dyeing cotton, wool, silk, mixed goods, straw, wood and paper, according to the methods used for the known substantive dyestuffs.

In witness whereof we have hereunto signed our names this 23rd day of December 1916, in the presence of two subscribing witnesses.

EUGEN ANDERWERT.
HERMAN FRITZSCHE.
HEINRICH SCHOBEL.

Witnesses:
CARL O. SPAMER,
AMAND RITTER.