

UNITED STATES PATENT OFFICE.

PAUL JULIUS, OF LUDWIGSHAFEN, GERMANY, ASSIGNOR TO BADISCHE ANILIN & SODA FABRIK, OF SAME PLACE.

ORANGE DYE AND PROCESS OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 679,172, dated July 23, 1901.

Application filed April 1, 1901. Serial No. 53,943. (No specimens.)

To all whom it may concern:

Be it known that I, PAUL JULIUS, a doctor of philosophy and a chemist, a subject of the Emperor of Austria-Hungary, residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria, Germany, have invented new and useful Improvements in Orange Dyes, of which the following is a specification.

My invention relates to the production of orange coloring-matter on the fiber by means of certain pyrazolone-carboxylic-acid derivatives.

I have found that phenyl-pyrazolone carboxylic acid, the so-called "tartrazinogen," (which can be obtained by saponifying the condensation product of phenyl-hydrazin and oxalyl-acetic ester, see W. Wislicenus, *Annalen*, Vol. 246, page 321,) combines readily with primulin sulfonic acid which has been diazotized on the fiber, giving rise to an orange tartrazin coloring-matter. In place of phenyl-pyrazolone carboxylic acid another homologous or analogous derivative thereof can be employed, such as can be prepared, for example, by condensing ortho or para tolyl-hydrazin, alpha or beta naphthyl-hydrazin, or para-nitro-phenyl-hydrazin with oxalyl-acetic ester and subsequent saponification of the condensation products thus obtained. The shades produced by combining these pyrazolone products with diazotized primulin sulfonic acid differ but little from one another. Those produced by means of the alpha-naphthyl-amin derivative are somewhat less bright than the others. In the present state of knowledge my new coloring-matter can be regarded as a mono-azo compound. The procedure for obtaining these new shades consists in diazotizing primulin sulfonic acid on the fiber of the material to be dyed in the known manner and then passing the goods thus treated through a solution of the phenyl-pyrazolone carboxylic acid chosen made alkaline by carbonate of soda. After leaving the goods in this solution for from ten (10) to twenty (20) minutes they are wrung out, rinsed, and otherwise treated as required.

I give an example of a method for obtaining pyrazolone bodies which can be used for the purposes of my invention; but I do not wish to claim the same.

Example: Heat together at a temperature of about one hundred (100°) degrees centigrade, twenty-one (21) parts of the sodium compound of oxalyl-acetic ester, sixteen (16) parts of ortho-tolyl-hydrazin hydrochlorid, and one hundred (100) parts of xylene for about one hour. Hydrazone formation appears to take place at first, and this is followed by further condensation. To complete the latter, add about one hundred and fifty (150) parts of water to the mixture, distil off the xylene by blowing in steam, and when no more hydrocarbon passes over add about eleven (11) parts of calcined soda to the mixture. Keep it boiling for about half ($\frac{1}{2}$) an hour longer by continuing to pass in steam, and then add about eleven and a half ($11\frac{1}{2}$) parts of caustic-soda solution, (containing about thirty-five per cent. of NaOH.) Heat on the boiling-water bath until the condensation product formed is saponified, filter from any resinous matter formed, cool, and precipitate the ortho-tolyl-pyrazolone carboxylic acid from the filtrate by carefully acidifying it with hydrochloric acid. The ortho-tolyl-pyrazolone carboxylic acid thus obtained can be purified by recrystallization from hot dilute alcohol. In a similar manner para-tolyl, alpha, and beta naphthyl, and para-nitro-phenyl-pyrazolone carboxylic acids can be prepared.

The mono-azo coloring-matter which I wish to claim generically and which can be obtained by combining diazotized primulin sulfonic acid with phenyl-pyrazolone carboxylic acid or one of its hereinbefore-mentioned derivatives is difficultly soluble to practically insoluble in cold water, as it contains but the sulfo group due to the primulin sulfonic acid. On reducing with zinc-dust and common-salt solution primulin sulfonic acid is regenerated. The shades obtained on cotton by means thereof are orange and are hardly altered by treatment with dilute carbonate-of-soda solution or dilute hydrochloric acid. They are exceeding fast to soap and light.

The mono-azo coloring-matter which I desire to claim specifically and which can be derived from diazotized primulin sulfonic acid and para-nitro-phenyl-pyrazolone carboxylic acid is difficultly soluble in cold water with

an orange color, the solution becoming redder on the addition of caustic-soda solution. On reduction with zinc-dust and common-salt solution primulin sulfonic acid is regenerated.

5 The shades obtained on cotton by means thereof are orange and are hardly altered by treatment with dilute carbonate-of-soda solution or dilute hydrochloric acid. They are also exceedingly fast to soap and to light.

10 The following example will serve to illustrate the nature of my invention and a manner of carrying it into practical effect; but my invention is not confined to the example. The parts are by weight.

15 Example: Dye one hundred (100) kilograms of cotton with three (3) kilograms of primulin sulfonic acid and diazotize the primulin sulfonic acid on the fiber in the well-known manner. Rinse the material thus treated in
20 cold water and pass it through a bath made up of ten (10) kilograms of para-nitro-phenyl-pyrazolone carboxylic acid and a sufficient excess of carbonate of soda in five thousand (5,000) liters of water. Allow the material
25 to remain in this bath for about twenty (20) minutes, rinse, and dry.

Now what I claim is—

1. The process of producing orange dye on the fiber by combining primulin sulfonic acid
30 which has been diazotized on the fiber with a hereinbefore-defined phenyl-pyrazolone-carboxylic-acid body, substantially as described.

2. The process of producing orange dye by combining diazotized primulin sulfonic acid
35 with a hereinbefore-defined phenyl-pyrazolone-carboxylic-acid body, substantially as described.

3. The process of producing orange dye by combining diazotized primulin sulfonic acid

with para-nitro-phenyl-pyrazolone carboxylic acid, substantially as described. 40

4. The new mono-azo dye which can be obtained from diazotized primulin sulfonic acid and a hereinbefore-defined phenyl-pyrazolone-carboxylic-acid body, which is difficultly
45 soluble to practically insoluble in cold water, which on reduction with zinc-dust and common-salt solution yields primulin sulfonic acid, and which when developed on the cotton fiber produces orange shades, which
50 shades are hardly altered on treatment with dilute carbonate-of-soda solution or with dilute hydrochloric acid and are exceedingly fast to light and soap, substantially as described. 55

5. The new mono-azo dye which can be obtained from diazotized primulin sulfonic acid and para-nitro-phenyl-pyrazolone carboxylic acid, which is difficultly soluble in cold water with an orange color which solution becomes
60 redder on the addition of caustic-soda solution and which on reduction with zinc-dust and common-salt solution yields primulin sulfonic acid, and which when developed on the cotton fiber produces orange shades which are
65 hardly altered on treatment with dilute carbonate-of-soda solution or on treatment with dilute hydrochloric acid and which are exceedingly fast to light and soap, substantially as described. 70

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

PAUL JULIUS.

Witnesses:

JOHN L. HEINKE,
JACOB ADRIAN.