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TETRAKISAZO-DYESTUFFS

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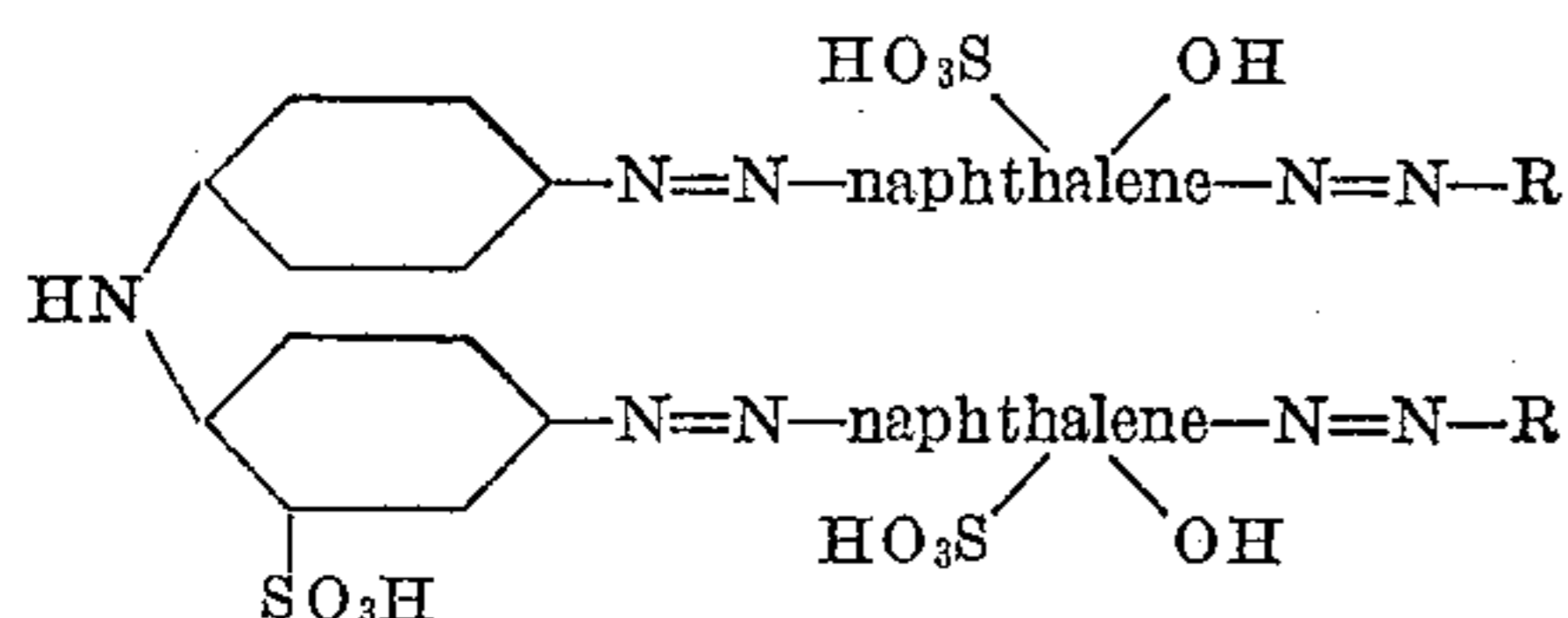
1

This invention relates to the preparation of tetrakisazo-dyestuffs of bloomy black shades having special value.

The tetrakisazo-dyestuff obtained by an alkaline coupling of the tetrazo compound of 4,4'-diamino-diphenylamine-2-sulfonic acid with 2 moles of 2-amino-8-hydroxynaphthalene-6-sulfonic acid further tetrazotising the disazo-dyestuff obtained and coupling the resulting tetrazo compound with 2 moles of 1,3-diaminobenzene, is of considerable technical importance to cotton and rayon dyeing because of its good dyeing properties. However a greenish black shade is obtained with it whereas in practice more bluish or violetish black shades are preferred.

Therefore attempts have already been made in modifying the dyestuff toward the desired direction. One route to this end is provided by German patent specification 704,772 describing the use of 1-hydroxyethylamino-3-aminobenzene or one of its derivatives (first described in German patent specification 476,910) instead of 1,3-diaminobenzene as final component. The procedure of German patent specification 704,772, however, provides only a relatively slight change of shade toward blue, due to the use of 1-hydroxyethylamino-3-aminobenzene.

It is the object of the present invention to prepare dyestuffs showing bloomy black shades of special value. These dyestuffs correspond to the general formula



(wherein one of the R's means an aromatic diamine of the group consisting of 1,3-diaminobenzene, 1,3-diaminotoluene, 1-hydroxyethylamino-3-aminobenzene, 1-hydroxyethylamino-3-aminotoluene, and the other R means a coupling component of the group consisting of 1,2-diaminobenzene and hydroxy and amino compounds of naphthalene).

Thus, according to the kind and quantity of the final components employed, it is possible to obtain variations of shade superior to those obtainable according to the procedure of German patent specification 704,772.

In addition, the possibility of obtaining the desired effects by use of technically readily available materials of very low cost as final compo-

2

nents, as 1,3-diaminobenzene or 2,4-diamino-1-methylbenzene and e. g. 1- or 2-hydroxynaphthalene, means a technical and economic advantage.

The success of the present procedure could not have been foreseen because the components being used besides 1,3-diaminobenzene and its derivatives yield, when employed by themselves, dyestuffs of inferior properties (e. g. insufficient affinity to the fibre) that cannot be used in practice.

The basis for the mixtures of final components used according to the present invention are on the one side chiefly 1,3-diaminobenzene, 1,3-diamino-6-methylbenzene and their hydroxyethylation products as obtained e. g. by treatment with glycol-chlorhydrin, as well as mixtures of these products.

As additional final components to be used according to this invention may be named 1- and 2-hydroxynaphthalene, 1-aminonaphthalene and its N-alkyl or aryl derivatives, diamino- and dihydroxynaphthalenes, aminohydroxynaphthalenes and their alkyl, aryl or acyl derivatives, N,N' - isopropylidenenaphthylenediamine - (1.8) and 1,2-diaminobenzene.

Possible middle-components of the naphthalene series are e. g.: 2-amino-8-hydroxynaphthalene-6-sulfonic acid, 1-amino-5-hydroxynaphthalene-7-sulfonic acid, 2-amino-5-hydroxynaphthalene-7-sulfonic acid, 1-amino-6-hydroxynaphthalene-3-sulfonic acid or mixtures of these components.

The following examples illustrate the invention but are not intended to limit it thereto; the parts are given by weight.

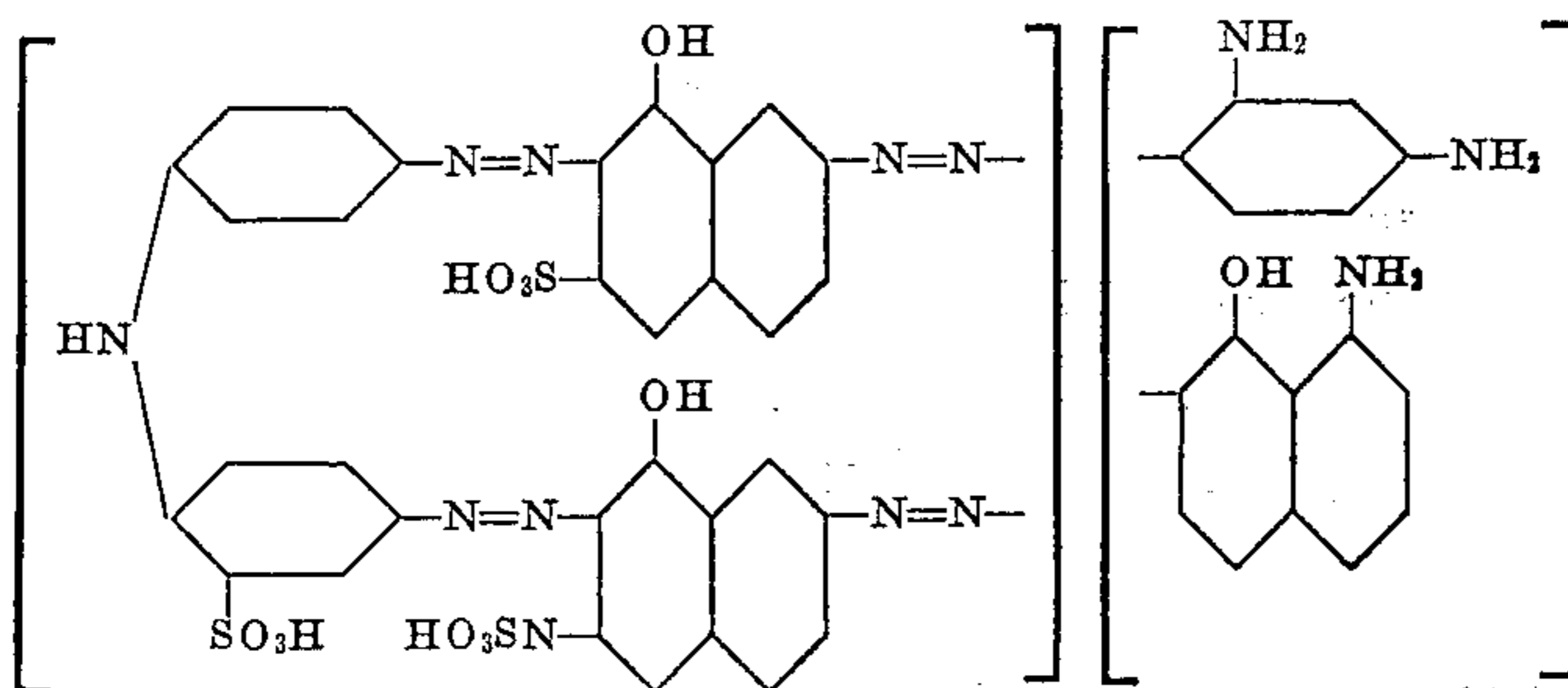
Example 1

29 kgs. of 4,4'-diaminodiphenylamine-2-sulfonic acid are dissolved in water and hydrochloric acid and, whilst cooling with ice, tetrazotized with sodium nitrite. The yellow tetrazo-solution is coupled with an alkaline solution of 47.8 kgs. of 2-amino-8-hydroxynaphthalene-6-sulfonic acid. When coupling completed the disazo-dyestuff is filtered off, eventually washed with a solution of sodium chloride of 2.5° Bé., repasted with ice water and further tetrazotized with hydrochloric acid and sodium nitrite. After removing the non-reacted nitrous acid the tetrazo compound is coupled with a mixture of 15.1 kgs. of 1,3-diaminobenzene and 7.6 kgs. of 1-amino-8-hydroxynaphthalene in an alkaline solution.

After separating and drying, a dark dyestuff powder is obtained soluble in water in the presence of sodium carbonate, which dyestuff dyes

3

cotton or rayon bloomy bluish to blue-violetish black shades. The dischargeability is very good. This dyestuff corresponds to the formula:



A similar dyestuff is obtained when using a mixture of 13 kgs. of 1,3-diaminobenzene and 10.8 kgs. of 1-amino-8-hydroxynaphthalene.

Example 2

The tetrazo compound of the disazo dyestuff, as obtained according to Example 1, is coupled with a mixture of 18 kgs. of 1,3-diaminobenzene dissolved in 300 litres of water, 2.9 kgs. of 1-hydroxynaphthalene dissolved in 25 litres of water, and 3 litres of caustic soda lye of 33° Bé. to which 36 kgs. of sodium carbonate are further added.

After heating moderately, filtering and drying a dark dyestuff powder is obtained, water soluble upon adding of soda solution and dyeing cotton or rayon from a soda-alkaline bath bloomy, bluish black shades. The dyeings have a very good dischargeability.

A tetrakisazo-dyestuff dyeing somewhat more violetish black shades is obtained when using in this example for the final coupling the alkaline solution of a mixture of 18.3 kgs. of 1,3-diaminobenzene, 1.1 kgs. of 1-hydroxynaphthalene and 1.1 kgs. of 2-hydroxynaphthalene.

When replacing the 2-amino-8-hydroxynaphthalene-6-sulfonic acid by 1-amino-5-hydroxynaphthalene-7-sulfonic acid a reddish black is obtained whereas with 2-amino-5-hydroxynaphthalene-7-sulfonic acid or 1-amino-6-hydroxynaphthalene-3-sulfonic acid more bluish black or navy blue shades are obtained which have similar properties.

On the other hand similar bluish or violetish black shades are obtained when using, for example, instead of 1-hydroxynaphthalene-2-amino-5-hydroxynaphthalene, 1,4- or 1,6-dihydroxynaphthalene, 1,8-diaminonaphthalene or N,N'-isopropylidenenaphthylenediamine-(1,8) in suitable quantities.

Example 3

The tetrazo compound of the disazo-dyestuff, as prepared according to Example 1, is coupled with the alkaline solution of a mixture of 8.6 kgs. of 1,3-diaminobenzene, 10.7 kgs. of 1,3-diamino-6-methylbenzene and 2.9 kgs. of 1-hydroxynaphthalene.

After working this up and drying, a dark, water soluble dyestuff powder is obtained, which dyes cotton or rayon full, bloomy black shades.

Example 4

29 kgs. of 4,4'-diaminodiphenylamine-2-sulfonic acid are dissolved with water and hydrochloric acid and tetrazotized with sodium nitrite. The yellow tetrazo solution is coupled with an alkaline solution of 47.8 kgs. of 2-amino-8-hydroxynaphthalene-6-sulfonic acid. When coupling completed, the disazo-dyestuff is filtered off, eventually washed with salt water of 2.5° Bé., re-

4

pasted with ice water and further tetrazotized with hydrochloric acid and sodium nitrite. After removal of the unused nitrous acid the tetrazo

compound is combined with the alkaline solution of a mixture of 17.3 kgs. of 1,3-diaminobenzene and 4.3 kgs. of 1,2-diaminobenzene.

After separating and drying, a dark water soluble powder is obtained which dyes cotton and rayon bloomy blue-black shades and else corresponds in its properties to the dyestuffs described in Examples 1-3.

Final coupling may also be carried out in the way of combining the tetrazo-disazo compound first with a solution of e. g. 2 to 3.5 kgs. of 1,2-diaminobenzene and, this being used up, with a solution of 17-20 kgs. of 1,3-diaminobenzene.

Example 5

29 kgs. of 4,4'-diaminodiphenylamine-2-sulfonic acid are dissolved with water and hydrochloric acid and, whilst cooling with ice, tetrazotized with sodium nitrite. The yellow tetrazo solution is coupled with an alkaline solution of 47.8 kgs. of 2-amino-8-hydroxynaphthalene-6-sulfonic acid. When coupling completed, the disazo dyestuff is filtered off, eventually washed with salt water of 2.5° Bé., repasted with ice water and further tetrazotized with hydrochloric acid and sodium nitrite. After removal of the unused nitrous acid, the tetrazo compound is combined with an alkaline solution of a mixture of 25.5 kgs. of a hydroxyethylated 1,3-diaminobenzene (as obtained by reacting 1 mole of glycolchlorhydrin on 1 mole of 1,3-diaminobenzene in an aqueous solution) and 2.9 kgs. of 1-naphthol.

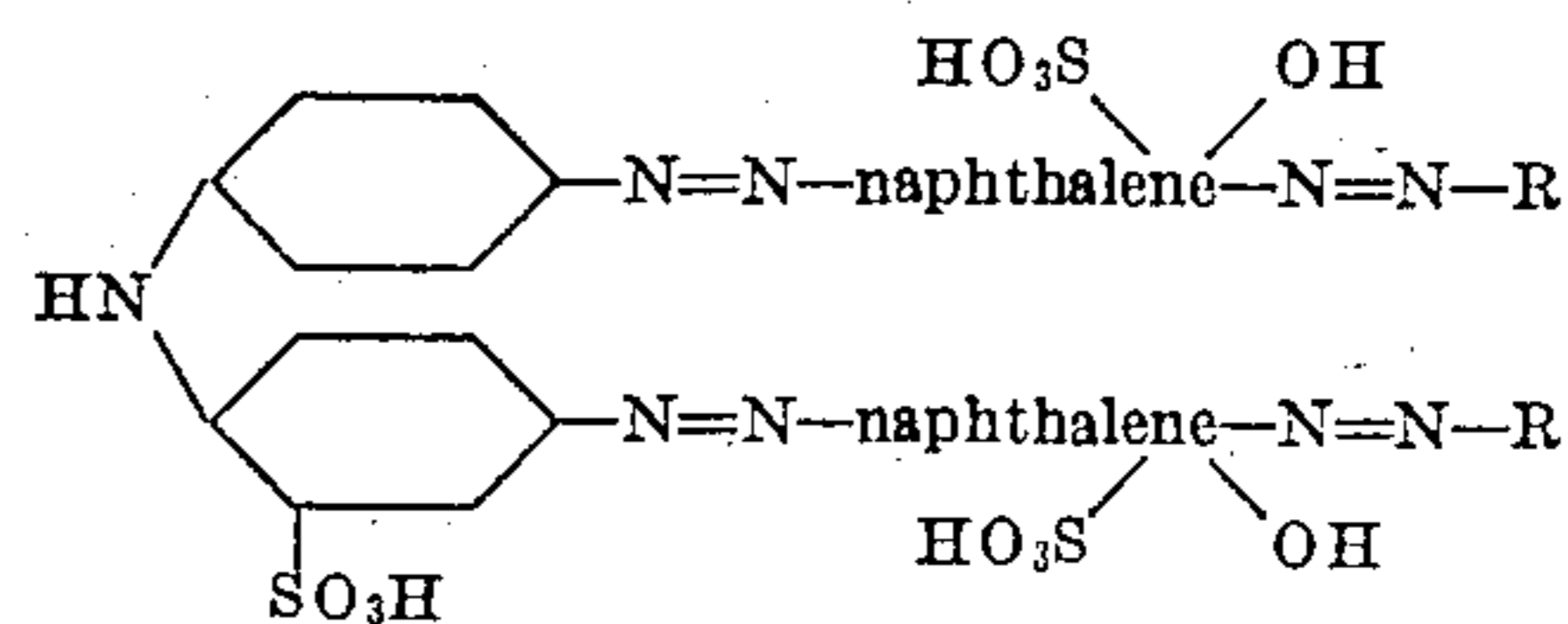
After separating and drying, a dark powder is obtained dyeing cotton and rayon bloomy blue-violetish black shades. The dyeings have a very good dischargeability.

A dyestuff similar in shade and properties is obtained when using for the final coupling a mixture of:

- 9.1 kgs. of 1,3-diaminobenzene
- 12.8 kgs. of the product obtained by reacting 1 mole of glycolchlorhydrin on 1 mole of 1,3-diaminobenzene in an aqueous solution and
- 2.9 kgs. of 1-naphthol.

I claim:

1. A tetrakisazo-dyestuff corresponding to the general formula

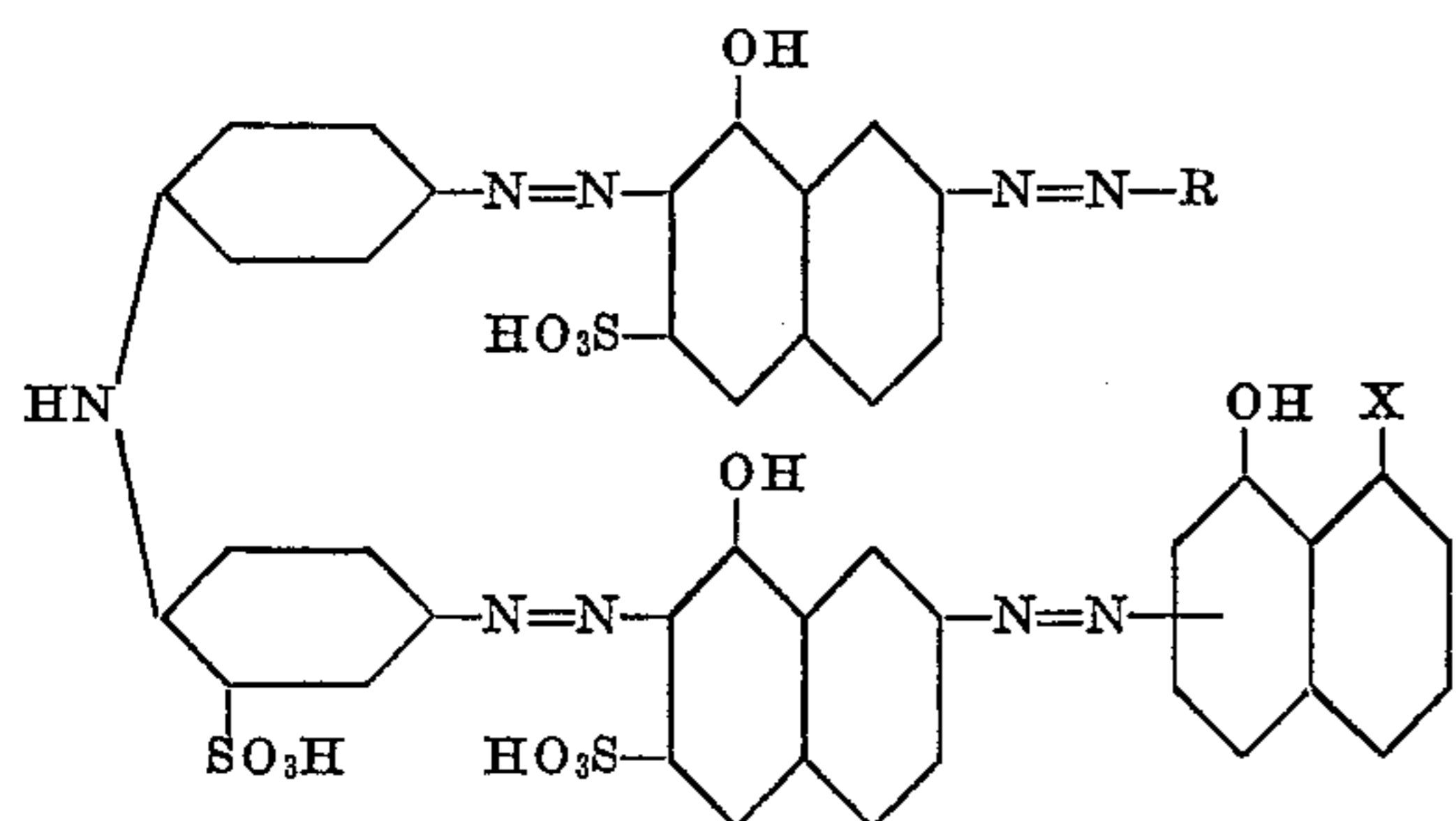


wherein one of the R's means an aromatic diamine of the group consisting of 1,3-diaminobenzene, 1,3-diaminotoluene, 1-hydroxyethylamino-3-aminobenzene, 1-hydroxyethylamino-3-amino-toluene, and the other R means a coupling com-

5

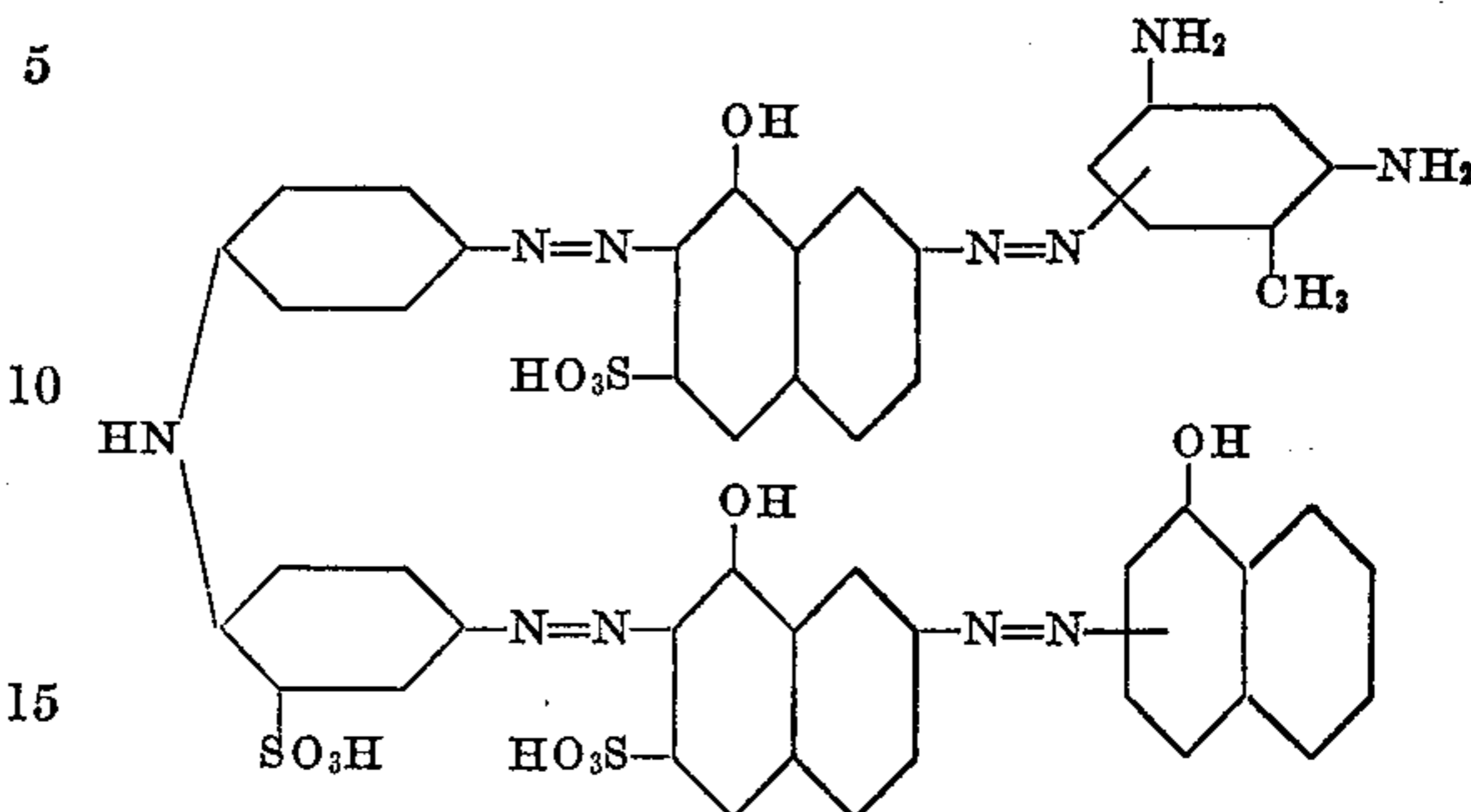
ponent of the group consisting of 1,2-diaminobenzene and hydroxy and amino compounds of naphthalene.

2. A tetrakisazo-dyestuff corresponding to the general formula

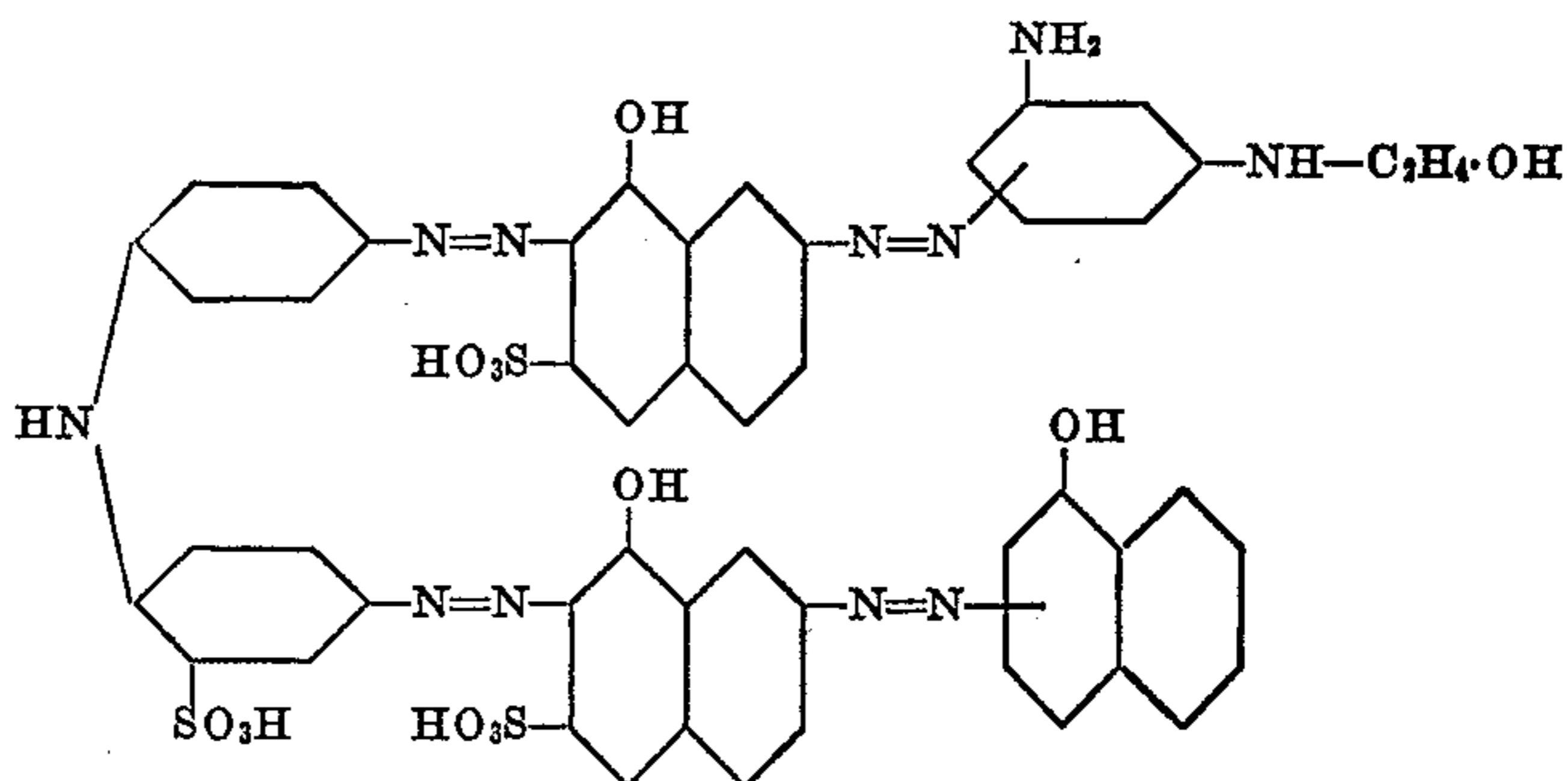


wherein R means an aromatic diamine of the group consisting of 1,3-diaminobenzene, 1,3-diaminotoluene, 1-hydroxyethylamino-3-amino-

4. The tetrakisazo-dyestuff corresponding to the formula

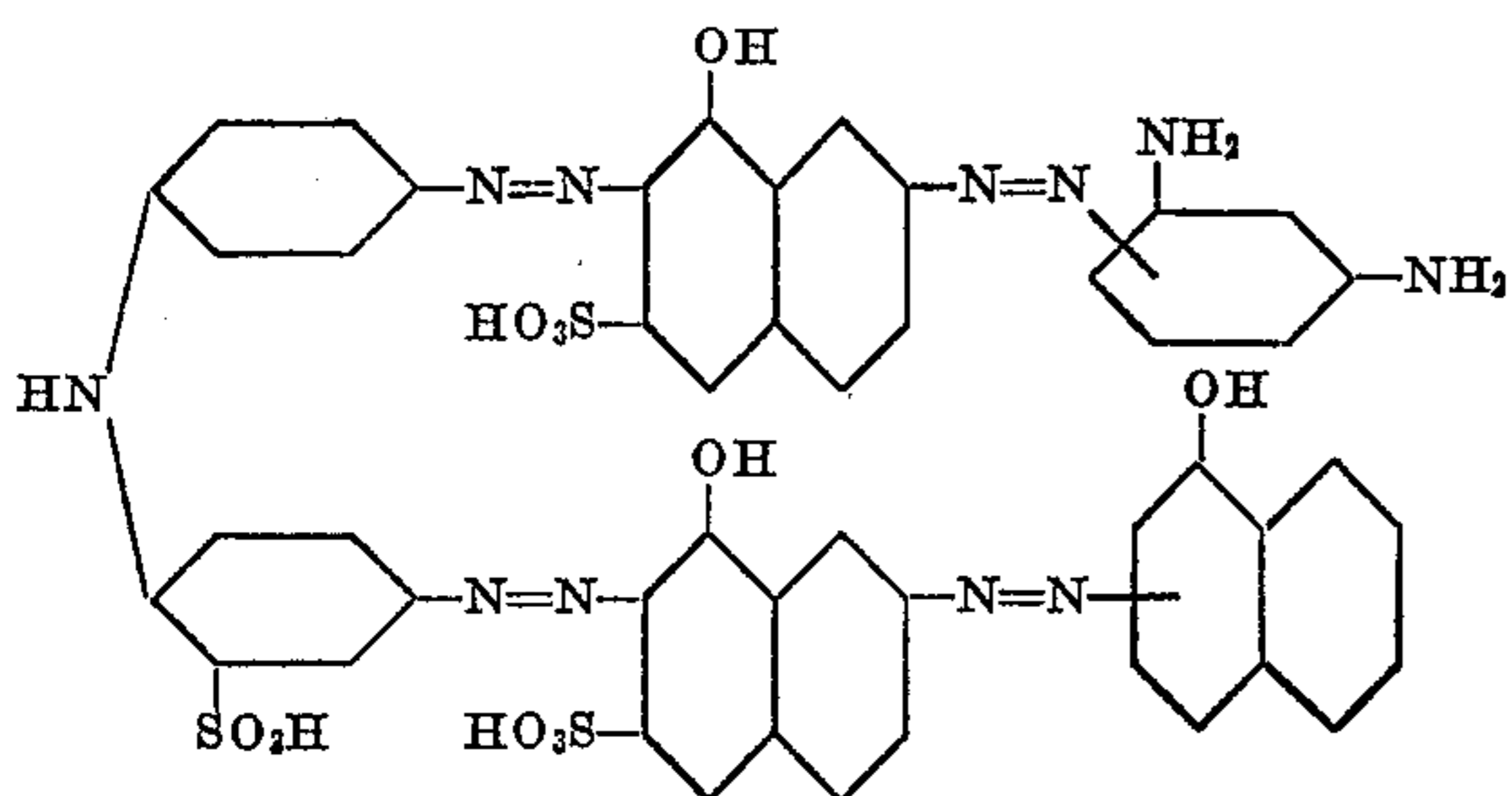


5. The tetrakisazo-dyestuff corresponding to the formula

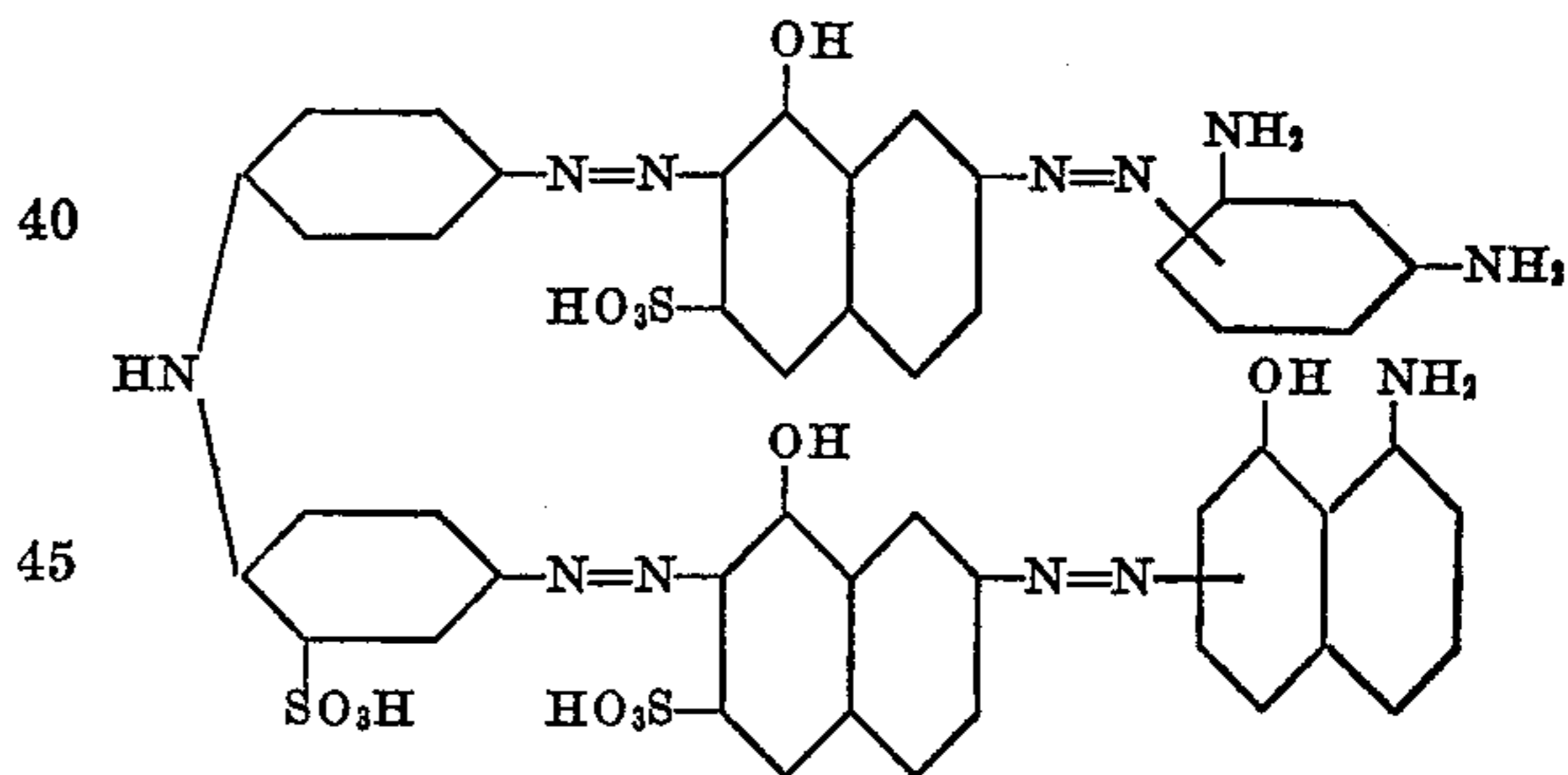


nobenzene, 1-hydroxyethylamino-3-amino-1,3-diaminobenzene, 1-hydroxyethylamino-3-amino-1,3-diaminobenzene and X means a radical of the group consisting of hydrogen and amino.

3. The tetrakisazo-dyestuff corresponding to the formula



6. The tetrakisazo-dyestuff corresponding to the formula



RICHARD FLEISCHHAUER.

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