

UNITED STATES PATENT OFFICE

2,265,433

INSOLUBLE AZO DYES

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No Drawing. Application January 29, 1941, Se-
rial No. 376,470. In Great Britain September
22, 1938

14 Claims. (Cl. 260—156)

This invention relates to new insoluble dye-
stuffs, to superior dyeings produced from said
dyestuffs and to methods of producing the same.

According to the invention we cause to inter-
act aminoarylpyridines with o-hydroxyaryl car-
boxylic acids, or with reactive derivatives of such
acids, in such a way that arylamides of the said
o-hydroxyaryl carboxylic acids are produced,
capable of coupling with diazonium compounds
in a position ortho to the hydroxy group.

Suitable o-hydroxyaryl carboxylic acids for
use in the above manner include 2:3-hydroxy-
naphthoic acid, 6-bromo- and 6-methoxy-2:3-
hydroxynaphthoic acids, 2:3-hydroxycarbazole
carboxylic acid, 2:3-hydroxy diphenylene oxide
carboxylic acid, and 2:3-hydroxyanthracene car-
boxylic acid.

The new arylamides are coupled with diazo-
nium compounds on cellulose fibers, such as
cotton, regenerated cellulose and similar dyeable
fibers, thereby dyeing the fiber. The arylamides
are convenient to dissolve and possess unusually
high affinity for cellulosic fiber when applied
thereto from aqueous caustic alkali solution.
The azoic colors produced on such fibers as the
result of coupling on the fiber with diazonium
compounds have good rubbing fastness and ex-
cellent general fastness properties. If desired,
the diazonium compounds may be applied in the
form of stable derivatives to develop the insol-
uble azo dyestuffs on the fiber.

The diazonium compounds employed may be
derived from aromatic amines commonly used
for making azoic colors such as, for example,
o- or m-chloroaniline, 4-chloro-2-aminoanisole
and 4-nitro-2-aminoanisole.

The invention is illustrated but not limited by
the following examples in which the parts are
by weight.

Example I

3 parts of N-(2'-hydroxy-3'-naphthoyl)-4-
alpha-pyridyl-aniline which contains some of
the corresponding beta and gamma compound
are made into a paste with 10 parts of Turkey
red oil neutralized with caustic soda and con-
taining 50% of water, and 60 parts of boiling
water are added, followed by 6 parts of aqueous
sodium hydroxide liquor of sp. gr. 1.30. The
solution is made up to 1,000 parts by adding 921
parts of cold water containing 10 parts of sodium
chloride. 50 parts of cotton yarn are soaked for
20 minutes in this solution, squeezed well and
immersed in 1,000 parts of a solution containing
2 parts of diazotized 5-nitro-2-amino-anisole.

The cotton is turned for 20 minutes, squeezed,
rinsed with cold water and then boiled in a solu-
tion containing 2 parts of sodium carbonate and
3 parts of soap per 1,000 parts. A bluish-red
shade is obtained having good fastness to chlo-
rine, kier boiling, boiling sodium carbonate solu-
tion and light. The following table affords a
list of further combinations together with the
shades produced which are obtained by replacing
the diazotized 5-nitro-2-amino-anisole in the
above example by other diazonium compounds.

Diazonium compound of—	Shade pro- duced
o-Chloraniline	Scarlet.
m-Chloraniline	Scarlet.
4-chloro-2-amino-anisole	Bluish-red.
5-chloro-2-amino-toluene	Red.
2:5-dichloraniline	Scarlet.
4-benzoylamino-2:5-diethoxyaniline	Blue.
4-nitro-2-amino-anisole	Red.
1-amino-anthraquinone	Red.
3-nitro-4-amino-toluene	Red.
4-chloro-2-nitroaniline	Red.

The coupling component used in this example
may be made as follows: 10 parts of 4-amino-
alpha-phenylpyridine mixed with the correspond-
ing beta and gamma compounds, the mixture
being made as described below, are dissolved in
175 parts of toluene, 11.0 parts of 2:3-hydroxy-
naphthoic acid are added and the solution is
stirred and heated to boiling under a reflux con-
denser. 3.0 parts of phosphorus trichloride are
added during 1 hour. The mixture is boiled for
a further 15 hours, cooled and poured into 100
parts of 10% aqueous solution of sodium car-
bonate. The toluene is driven off by distillation
in steam. The substance remaining undissolved
in the aqueous sodium carbonate is then filtered
off and dissolved in a sufficiency of aqueous
sodium hydroxide solution. After filtration of
the solution when necessary, the new compound
is precipitated by the addition of acid, filtered
off, washed with water and dried. The product
is N-(2'-hydroxy-3'-naphthoyl)-4-alpha-pyri-
dyl-aniline mixed with the corresponding beta
and gamma compounds, and has a high affinity
for cellulosic fiber.

The mixture of 4-amino-alpha-phenylpyridine
and the corresponding beta and gamma com-
pounds used above is made by reacting pyridine
with diazotized 1-amino-4-nitrobenzene accord-
ing to the method described in British applica-
tion No. 26,064/38 and reducing the mixture of
isomeric 4-nitrophenylpyridines so obtained.

Example II

A dye bath was made in the manner described in Example I by using an equivalent amount of N-(2'-hydroxy-3'-carbazole-carbonyl)-4-pyridyl-aniline instead of 3 parts of N-(2'-hydroxy-3'-naphthoyl)-4-alpha-pyridyl-aniline. Cotton yarn was dyed in the bath and developed with 5-nitro-2-amino-anisole in the manner described in Example I. A brown shade having excellent fastness properties was obtained.

Development of the direct dyeing made with N-(2'-hydroxy-3'-carbazole-carbonyl)-4-pyridyl-aniline with 4-nitro-2-amino-toluene gave a brown shade. Development with 4-chloro-2-amino-anisole gave a brown shade and development with 4-benzoylamino-2,5-diethoxy-aniline gave a dark reddish blue shade. All of these dyeings had excellent fastness properties similar to those of the dyeing described in Example I.

By using N-(2'-hydroxy-3'-carbazole-carbonyl)-4-picolyl-aniline instead of the corresponding pyridyl aniline, a dyeing having a brown shade and excellent fastness properties was produced. Instead of using the picolyl aniline, the aryl-substituted methyl-, methoxy-, nitro- or chloro-picolyl derivatives can be used. These anilides give dyeings having excellent fastness properties in modified shades.

Example III

By making the direct dyeing with N-(2'-hydroxy-3'-naphthoyl)-4-pyridyl-2-methyl-aniline and similarly developing, dyeings having excellent fastness properties were produced on cotton fiber as follows:

Diazonium compound of—	Shade produced
5-nitro-2-amino-anisole.....	Red.
4-nitro-2-amino-toluene.....	Red.
5-chloro-2-amino-toluene.....	Red.
3-nitro-4-amino-toluene.....	Red.
1-amino-anthraquinone.....	Red.

Example IV

By dyeing cotton fibers with N-(2'-hydroxy-3'-naphthoyl)-4-picolyl-aniline in accordance with the procedure of Example I instead of the pyridyl aniline described therein and then developing with 5-nitro-2-amino-anisole, the fibers were dyed a red shade having other properties similar to those of the dyeings of Example I.

Example V

A dye bath was made in accordance with the procedure of Example I using N-(2'-hydroxy-3'-diphenylene-oxide-carbonyl)-4-pyridyl-aniline instead of N-(2'-hydroxy-3'-naphthoyl)-4-alpha-pyridyl-aniline. A direct dyeing was made on cotton fibers and the color was developed with diazotized 5-nitro-2-amino-anisole. A dyeing in a brown shade having excellent fastness properties was produced.

As illustrative of other anilides which may be used to the same effect as those described in the above examples are mentioned the derivatives of N-(2'-hydroxy-3'-diphenylene-oxide-carbonyl)-4-pyridyl-aniline which are substituted in the benzene nucleus of the phenyl pyridine group by methyl, methoxy, nitro or chloro; the anilides derived from 2-hydroxy-3-diphenylene-oxide-carboxylic acid and 4-picolyl-aniline or the derivatives thereof which are substituted in the benzene nucleus by methyl, methoxy, nitro or chloro; the anilides derived from 6-bromo or

6-methoxy-2,3-hydroxy-naphthoic acid and 4-pyridyl- or 4-picolyl-anilines; the anilides derived from 2,3-hydroxy-anthracene-carboxylic acid and 4-pyridyl- or 4-picolyl-anilines.

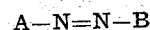
Many diazo components besides those mentioned can be used to produce dyeings having the described properties, namely any primary arylamine of the benzene or naphthalene series which is devoid of solubilizing groups, such as those used for making azoic colors.

This is a continuation-in-part of our application Serial No. 295,912, filed September 21, 1939.

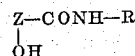
From the foregoing disclosure it will be recognized that the invention is susceptible of modification without departing from the spirit and scope thereof and it is to be understood that the invention is not restricted to the specific illustrations thereof herein set forth.

We claim:

1. Compounds having the formula



in which A represents one of a group consisting of the radicals of 1-amino-anthraquinone and the primary arylamines of the benzene series which are devoid of solubilizing groups; and B is the radical of a coupling component represented by the formula



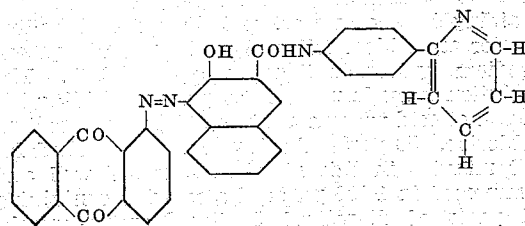
in which the hydroxy and the group —CONHR are in ortho positions to each other and wherein Z is one of a group consisting of the radicals of naphthalene, the 6-bromo and 6-methoxy derivatives thereof, carbazole, diphenylene oxide and anthracene; and R is from the group consisting of the radicals of C-phenyl pyridine, C-phenyl picoline and the methyl, methoxy, nitro and chloro aryl-substituted derivatives of said pyridine and picoline.

2. An azo compound having as diazo component one of a group consisting of the radical of 1-amino-anthraquinone and the radicals of primary arylamines of the benzene series which are devoid of solubilizing groups coupled to the radical of a pyridyl-anilide of 2-hydroxy-3-naphthoic acid.

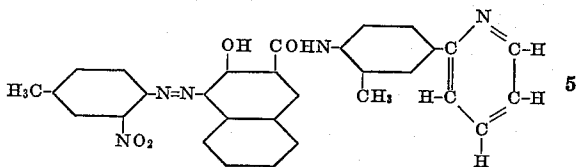
3. An azo compound having as diazo component one of a group consisting of the radical of 1-amino-anthraquinone and the radicals of primary arylamines of the benzene series which are devoid of solubilizing groups coupled to the radical of a pyridyl-ortho-toluidide of 2-hydroxy-3-naphthoic acid.

4. An azo compound having as diazo component one of a group consisting of the radical of 1-amino-anthraquinone and the radicals of primary arylamines of the benzene series which are devoid of solubilizing groups coupled to the radical of a pyridyl anilide of 2-hydroxy-carbazole-3-carboxylic acid.

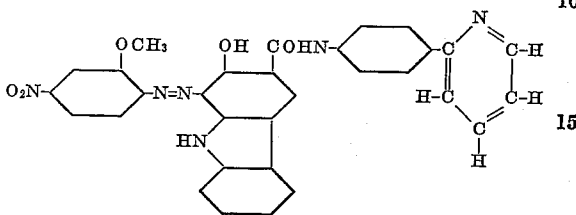
5. The compound represented by the formula



6. The compound represented by the formula



7. The compound represented by the formula



8. Cellulosic fibers dyed with the compound of claim 1.

9. Cellulosic fibers dyed with the compound of claim 2.

10. Cellulosic fibers dyed with the compound of claim 3.

11. Cellulosic fibers dyed with the compound of claim 4.

12. Cellulosic fibers dyed with the compound of claim 5.

13. Cellulosic fibers dyed with the compound of claim 6.

14. Cellulosic fibers dyed with the compound of claim 7.

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