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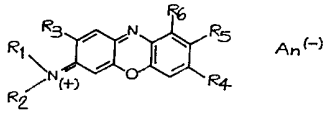
(72) Inventor HUBERTUS PSAAR

(54) PROCESS FOR THE PREPARATION OF OXAZINE DYESTUFFS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The subject of the invention is a process for the production of basic oxazine dyestuffs.

According to the present invention we provide a process for the production of an oxazine dyestuff of the general formula



(I)

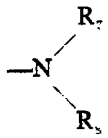
wherein

R_1 denotes hydrogen or optionally substituted alkyl or alkenyl,

R_2 denotes optionally substituted alkyl, alkenyl, aryl or aralkyl,

R_3 denotes hydrogen, alkyl or alkoxy,

R_4 denotes hydrogen or the group



R_5 denotes hydrogen, alkyl or alkoxy,

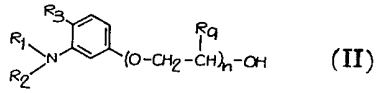
R_6 denotes hydrogen or, conjointly with R_5, forms a fused aromatic ring,

R_7 denotes hydrogen or optionally substituted alkyl or alkenyl,

R_8 denotes hydrogen or optionally substituted alkyl, alkenyl, aryl or aralkyl and

$An^{(-)}$ denotes an anion, in which the above-mentioned optionally substituted alkyl radicals are optionally substituted other than by an aryl radical, in which an optionally substituted 3 - (β - hydroxyalkoxy or ω - hydroxy - polyalkoxy) - aryl - amine is nitrosated in aqueous solution in the presence of an acid and the resulting nitroso compound is subsequently subjected to a condensation reaction with an optionally substituted phenol.

A preferred reaction is carried out by nitrosation of aminophenol ethers of the general formula



(II)

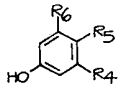
wherein

R_1, R_2 and R_3 have the abovementioned meaning and

R_9 denotes hydrogen or alkyl and

n denotes 1, 2 or 3,

in the presence of an acid which supplies the anion $An^{(-)}$ and subsequent reaction of the product with compounds of the formula



(III)

wherein

R_4, R_5 and R_6 have the abovementioned meaning.

The alkyl groups have, in particular, 1—4 carbon atoms and the alkenyl groups have 2 or 3 carbon atoms. Suitable substituents of the alkyl groups are, for example, hydroxyl, C_1—C_4-alkoxy, cyano, C_1—C_4-alkoxycarbonyl or aminocarbonyl. Preferred alkoxy groups are C_1—C_4-alkoxy groups.

Aryl is understood as preferably phenyl, and aralkyl as preferably benzyl.

The benzene ring and the naphthalene ring may be mentioned above all as aromatic rings which can be formed by R_5 and R_6 conjointly.

The phenyl groups and the benzene or naphthalene rings can, in turn, be substituted by non-ionic groups and/or carboxyl groups.

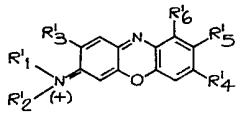
Non-ionic substituents in the sense of the invention are the non-dissociating substituents customary in dyestuff chemistry, such as halogen and alkyl, cycloalkyl, hydroxyl, alkoxy, aralkoxy, cycloalkoxy, aryloxy, acyloxy, acylalkoxycarbonyl, aminocarbonyl, nitrile, amino, alkylamino, dialkylamino, acylamino, aminosulphonyl, mercapto, alkylmercapto and arylmercapto groups.

The aromatic rings are preferably substituted by 1 or 2 halogen atoms or C_1—C_4-alkyl or C_1—C_4-alkoxy groups.

Possible anions are all the organic and inorganic anions customary for cationic dyestuffs. Colourless anions are preferred.

The anion is determined by the process of preparation and any purification of the dyestuffs which may be carried out. Preferably, the dyestuffs are in the form of halides and especially of chlorides. The anions can be replaced, in a known manner, by other anions, for example methosulphate, ethosulphate, sulphate, benzenesulphate or toluenesulphate or acetate.

The new process can be used in particular for the preparation of dyestuffs of the formula



(IV)

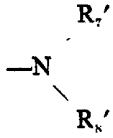
wherein

R_1' denotes hydrogen, C_1—C_4-alkyl, C_2- or C_3-alkenyl, β-cyanoethyl, β-hydroxyethyl, β-hydroxypropyl, β-chloroethyl, β-C_1—C_4-alkoxyethyl, β-C_1—C_4-alkoxypropyl or β-carbamoylethyl,

R_2' denotes C_1—C_4-alkyl, C_2- or C_3-alkenyl, β-cyanoethyl, β-hydroxyethyl, β-hydroxypropyl, β-chloroethyl, β-C_1—C_4-alkoxyethyl, β-C_1—C_4-alkoxypropyl or β-carbamoylethyl, or phenyl or benzyl which are optionally substituted by C_1—C_4-alkyl, halogen or C_1—C_4-alkoxy,

R_3' denotes hydrogen, C_1—C_4-alkyl or C_1—C_4-alkoxy,

R_4' denotes hydrogen or the group



R_5' denotes hydrogen, C_1—C_4-alkyl or C_1—C_4-alkoxy,

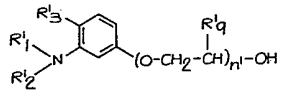
R_6' denotes hydrogen or, together with R_5', denotes a benzene ring,

R_7' denotes hydrogen, C_1—C_4-alkyl, C_2- or C_3-alkenyl, β-cyanoethyl, β-hydroxyethyl, β-hydroxypropyl, β-chloroethyl, β-C_1—C_4-alkoxyethyl, β-C_1—C_4-alkoxypropyl or β-carbamoylethyl,

R_8' denotes hydrogen, C_1—C_4-alkyl, C_2 or C_3-alkenyl, β-cyanoethyl, β-hydroxyethyl, β-hydroxypropyl, β-chloroethyl, β-C_1—C_4-alkoxyethyl, β-C_1—C_4-alkoxypropyl or β-carbamoylethyl, or phenyl or benzyl which are optionally substituted by C_1—C_4-alkyl, halogen or C_1—C_4-alkoxy and

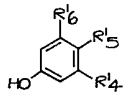
$An^{(-)}$ denotes an anion,

from nitroso compounds of aminophenol ethers of the formula



(V)

and compounds of the formula



(VI)

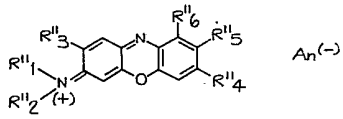
In the formulae (V) and (VI),

the radicals R_1' to R_6' have the above-mentioned meaning and

R_9' represents hydrogen, methyl or ethyl and

n' represents 1 or 2.

Amongst the dyestuffs of the formula (IV), those of the formula



(VII)

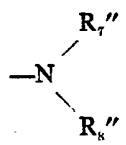
wherein

R_1'' denotes hydrogen, methyl or ethyl,

R_2'' denotes methyl, ethyl, cyanoethyl or phenyl which is optionally substituted by methyl, chlorine or methoxy,

R_3'' denotes hydrogen, methyl or methoxy,

R_4'' denotes hydrogen or the group



R_5'' denotes hydrogen, methyl or methoxy,

R_6'' denotes hydrogen,

R_7'' denotes hydrogen, methyl or ethyl and

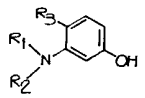
R_8'' denotes hydrogen, methyl, ethyl, cyano-

ethyl or phenyl which is optionally substituted by methyl, chlorine or methoxy, and

$An^{(-)}$ has the indicated meaning,

can be prepared particularly advantageously.

Amino-ethers of the formula (II) have been described, for example, by D. R. Boyd and E. R. Marle in Journal of the Chemical Society 105 (1914), pages 2117—2139). They can be prepared by reacting aminophenols of the formula



(VIII)

wherein

R_1, R_2 and R_3 have the abovementioned meaning, with epoxides.

The conversion of the aminophenols (VIII) is carried out in the presence of small amounts of an alkali at temperatures of 80—120°C.

Suitable epoxides are, preferably, ethylene oxide, propylene oxide and butylene oxide. The resulting reaction mixture can be further processed either direct or after purification.

The nitrosation of the aminophenol ethers (II) is carried out in an aqueous acid solution, for example in hydrochloric acid, with sodium nitrite. The resulting nitroso compounds possess an excellent solubility in water. They do not need to be isolated from the reaction medium prior to the condensation reaction with the compounds (III). The compounds (III) are employed in the condensation reaction preferably in alcoholic, for example methanolic, solution. The condensation reaction is preferably carried out at temperatures of 60—80°C.

The dyestuffs of the formula (I) can be isolated from the reaction medium by known processes, for example by precipitation with zinc chloride or, after removal of the solvent, by precipitation with urea, in accordance with the process of German Offenlegungsschrift (German Published Specification) 2,353,987.

Example 1.

165 parts by weight of 3-diethylaminophenol and 2 parts by weight of triethanolamine are warmed to 90°C under nitrogen. 55 parts by weight of ethylene oxide are then introduced in the course of 1 hour, whilst stirring. The mixture is stirred for a further 2 hours at 90°C and cooled to room temperature and the ethylene oxide is blown off with nitrogen.

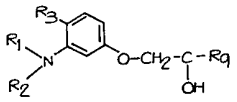
243 parts by weight of a reaction product which contains 86% of 3 - diethylaminophenyl β-hydroxyethyl ether are obtained. The ether can be employed without further purification for synthesis of the dyestuff, in accordance with Example 8.

The purification and isolation of the ether is effected by distillation. It has a boiling point of 186—189°C/13 mm. It was identified by the IR and NMR spectra (Figures 1 and 2).

If 65 parts by weight of propylene oxide are used in place of ethylene oxide, 3-diethylamino-phenyl β-hydroxypropyl ether is obtained.

The aminophenol ethers listed in Table 1 were prepared in the same way.

TABLE 1



Example	R_1	R_2	R_3	R_9
2	CH_3	CH_3	CH_3	CH_3
3	CH_3	CH_3	H	H
4	C_2H_5	H	CH_3	CH_3
5	CH_3	C_2H_4CN	H	CH_3
6	H	C_2H_4CN	OCH_3	CH_3
7	H	$C_6H_5OCH_3$	H	H

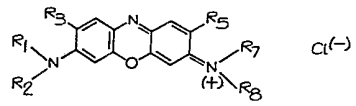
Example 8.

488 parts by weight of sodium nitrite, dissolved in 735 parts by weight of water, are allowed to run into a solution of 191 parts by weight of 3-diethylaminophenyl β-hydroxypropyl ether (70%), 188 parts by weight of hydrochloric acid (30%) and 145 parts by weight of water at 0—5°C. After the mixture has been stirred for 1 hour, the aqueous solution of the nitroso compound is allowed to run slowly into a solution of 99 parts by weight of 3-diethylaminophenol in 475 parts by weight of methanol at 70—75°C. After the reaction has ended, the mixture is cooled to 50°C and the dyestuff is precipitated with 50 parts by weight of zinc chloride. The dyestuff is filtered off at 20°C in the form of the zinc chloride double salt and is rinsed with methanol.

In a modified form, the dyestuff can also be isolated with urea by distilling off the methanol and water in vacuo after the reaction has ended, adding 600 parts by weight of anhydrous alcohol, 180 parts by weight of urea and 18 parts by weight of hydrochloric acid, cooling the mixture to 0°C and filtering off the dyestuff in the form of the urea adduct.

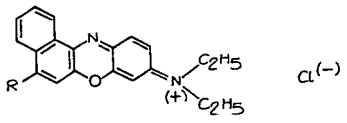
The dyestuffs listed in the table which follows were prepared by the same procedure:

TABLE 2



Example	R_1	R_2	R_3	R_7	R_8	R_5
9	CH_3	CH_3	H	CH_3	CH_3	H
10	C_2H_5	C_2H_5	H	H	C_2H_5	CH_3
11	C_2H_5	C_2H_5	H	H	C_2H_4CN	CH_3
12	C_2H_5	C_2H_5	H	H	C_2H_4CN	OCH_3
13	C_2H_5	C_2H_5	H	CH_3	C_2H_4CN	H
14	C_2H_5	C_2H_5	H	CH_3	CH_3	CH_3
15	C_2H_5	C_2H_5	H	H	C_6H_5	H
16	CH_3	CH_3	CH_3	C_2H_5	C_2H_4CN	H
17	C_2H_5	H	CH_3	CH_3	CH_3	CH_3
18	C_2H_5	H	CH_3	H	H	OCH_3
19	H	$C_6H_5OCH_3$	H	H	C_2H_4CN	CH_3
20	H	C_6H_5	CH_3	H	C_2H_5	CH_3

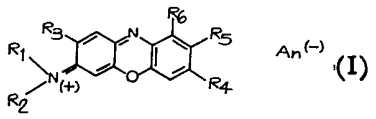
TABLE 3



Example	R
21	H
22	NH_2
23	$N(C_2H_5)_2$

WHAT WE CLAIM IS:—

1. A process for the production of a basic oxazine dyestuff of the general formula



(I)

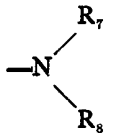
in which

R_1 denotes a hydrogen atom or an optionally substituted alkyl or alkenyl group,

R_2 denotes an optionally substituted alkyl, alkenyl, aryl or aralkyl group,

R_3 denotes a hydrogen atom or an alkyl or alkoxy group,

R_4 denotes a hydrogen atom or a group of the general formula



R_5 denotes a hydrogen atom or an alkyl or alkoxy group,

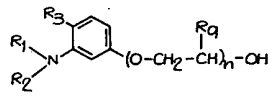
R_6 denotes a hydrogen atom or, conjointly with R_5, forms a fused aromatic ring,

R_7 denotes a hydrogen atom or an optionally substituted alkyl or alkenyl group, and

R_8 denotes a hydrogen atom or an optionally substituted alkyl, alkenyl, aryl or aralkyl group in which the above-mentioned optionally substituted alkyl radicals are optionally substituted other than by an aryl radical,

in which an optionally substituted 3 - (β-hydroxyalkoxy or ω - hydroxy - polyalkoxy)-arylamine is nitrosated in aqueous solution in the presence of an acid and the resulting nitroso compound is subsequently subjected to a condensation reaction with an optionally substituted phenol.

2. A process according to Claim 1, in which an aminophenol ether of the general formula



(II)

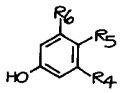
in which

R_1, R_2 and R_3 have the same meaning as in Claim 1,

R_9 denotes a hydrogen atom or an alkyl group and

n is 1, 2 or 3,

is nitrosated and the reaction product is subjected to a condensation reaction with a phenol of the general formula

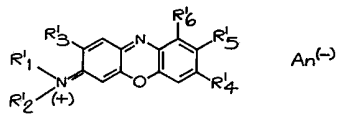


(III)

in which

R_4, R_5 and R_6 have the same meanings as in Claim 1.

3. A process according to Claim 1, for the production of a compound of the general formula



(IV)

in which

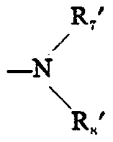
R_1' denotes a hydrogen atom or a C_1 to C_4 alkyl, C_2- or C_3-alkenyl, β-cyanoethyl, β - hydroxyethyl, β - hydroxypropyl, β-chloroethyl, β-C_1 to C_4 alkoxyethyl, β-C_1 to C_4 alkoxypropyl or β-carbamoylethyl,

R_2' denotes a C_1 to C_4 alkyl, C_2- or C_3-alkenyl, β-cyanoethyl, β-hydroxyethyl, β-hydroxypropyl, β-chloroethyl, β-C_1 to C_4 alkoxyethyl, β-C_1 to C_4 alkoxypropyl or β-carbamoylethyl group, or a phenyl or

benzyl group, which is optionally substituted by C_1 to C_4 alkyl, halogen or C_1 to C_4 alkoxy,

R_3' denotes a hydrogen atom or a C_1 to C_4 alkyl or C_1 to C_4 alkoxy group,

R_4' denotes a hydrogen atom or a group of the general formula



R_5' denotes a hydrogen atom, a C_1 to C_4 alkyl or C_1 to C_4 alkoxy group,

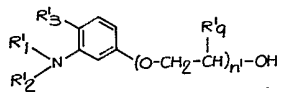
R_6' denotes a hydrogen atom or, together with R_5' denotes a benzene ring,

R_7' denotes a hydrogen atom or a C_1 to C_4 alkyl, C_2- or C_3-alkenyl, β-cyanoethyl, β - hydroxyethyl, β - hydroxypropyl, β-chloroethyl, β-C_1 to C_4 alkoxyethyl, β-C_1 to C_4 alkoxypropyl or β-carbamoylethyl,

R_8' denotes a hydrogen atom, C_1 to C_4 alkyl, C_2- or C_3-alkenyl, β-cyanoethyl, β-hydroxyethyl, β-hydroxypropyl, β-chloroethyl, β-C_1 to C_4 alkoxyethyl, β-C_1 to C_4 alkoxypropyl or β-carbamoylethyl group, or a phenyl or benzyl group which is optionally substituted by C_1 to C_4 alkyl, halogen or C_1 to C_4 alkoxy, and

$An^{(-)}$ denotes an anion,

in which an aminophenol ether of the general formula



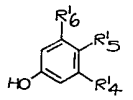
(V)

in which n' is 1 or 2,

R_1', R_2', and R_3' have the above-mentioned meanings, and

R_9' denotes a hydrogen atom or a methyl or ethyl group,

is nitrosated and the reaction product is subjected to a condensation reaction with a phenol of the general formula



(VI)

in which

R_4', R_5' and R_6' have the above-mentioned meanings.

4. A process according to Claim 3, in which

R_1' denotes a hydrogen atom or a methyl or ethyl group,

R_2' denotes a methyl, ethyl or cyanoethyl group or a phenyl group which is optionally substituted by methyl, chlorine or methoxy,

R_3' denotes a hydrogen atom or a methyl or methoxy group,

R_4' has the same meaning as in Claim 3,

R_5' denotes a hydrogen atom or a methyl or methoxy group,

R_6' denotes a hydrogen atom,

R_7' denotes a hydrogen atom or a methyl or ethyl group and

R_8' denotes a hydrogen atom or a methyl, ethyl or cyanoethyl group or a phenyl group which is optionally substituted by methyl, chlorine or methoxy.

5. A process according to Claim 1, when carried out substantially as hereinbefore described in respect of any of Examples 8 to 23.

6. A basic oxazine dyestuff when produced by the process of any of the foregoing claims.

For the Applicants,
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1570109 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

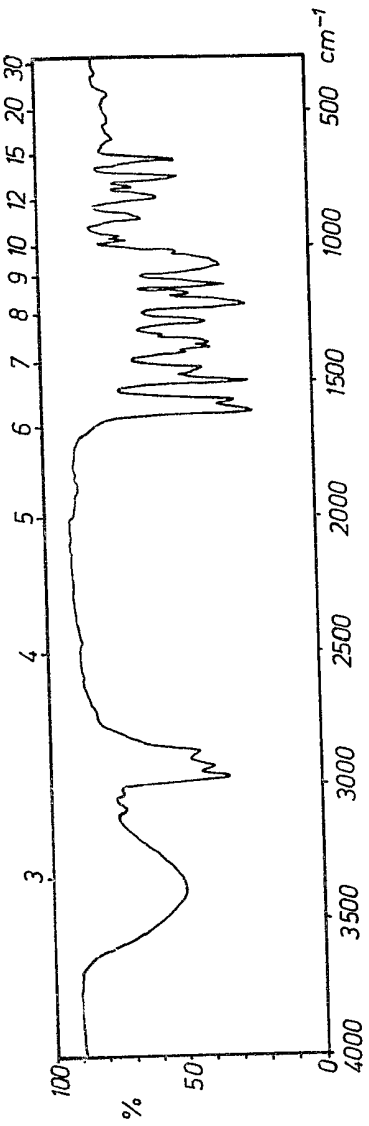

FIG. 1

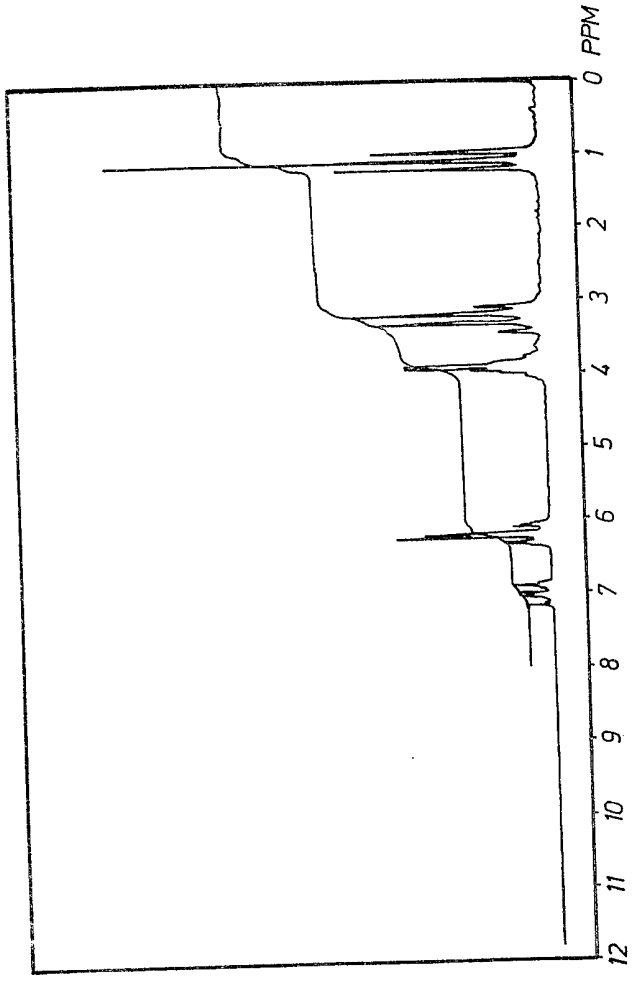

FIG. 2