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Asymmetric dioxazine compounds and method for dyeing or printing fiber materials using the same

Unsymmetrische Dioxazinverbindungen und Verfahren zum Färben oder Bedrucken von Fasermaterialien mittels derselben

Composés dioxazines asymétriques et procédé pour colorer ou imprimer des matériaux fibreux utilisant ceux-ci

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The present invention relates to asymmetric dioxazine compounds suitable for use in dyeing and printing materials containing hydroxyl groups and/or amide groups, particularly those such as cellulose fiber, natural and synthetic polyamide fibers, polyurethane fiber, leather and mixed yarns thereof, to obtain dyed or printed products of a color fast to light, wetness and chlorine.

There are known some reactive dyes having a dioxazine skeleton in their molecular structure. For instance, US-A-4,780,107 and US-A-4,933,446 disclose symmetric dioxazine compounds while GB-A-1,477,071 and US-A-4,566,742 refer to asymmetric dioxazine dyes. However, they are yet insufficient in dye performances, such as level dyeing property, build-up property, dyeing velocity and fastness properties, particularly such as chlorine fastness. Particularly, in case of dyeing or printing the hydroxyl group-containing fiber materials, fastness properties of dyed or printed products, particularly such as chlorine fastness, is not satisfactory. The present inventors have conducted extensive studies, and as a result, asymmetric dioxazine compounds capable of solving the above-mentioned problem have been found.

The present invention provides certain asymmetric dioxazine compounds represented by the following formula (I) in the free acid form:

\[
\begin{align*}
\text{R}_3 & \quad (\text{SO}_3\text{H})^\epsilon_n \\
\text{R}_4 & \quad (\text{A}_1)^n \\
\text{X}_1 & \quad \text{SO}_3\text{H} \\
\text{SO}_3\text{H} & \quad \text{X}_2 \\
\text{N} & \quad \text{W} \\
\text{W} & \quad \text{N} \\
\text{N} & \quad \text{Z} \\
\text{R}_1 & \quad (\text{A}_2)^m \\
\end{align*}
\]

wherein \(\text{A}_1\) and \(\text{A}_2\) independently of one another are each sulfo, halo, alkyl or alkoxy. \(\text{W}\) is an unsubstituted or substituted aliphatic or aromatic bridging group. \(\text{X}_1\) and \(\text{X}_2\) independently of one another are each hydrogen, halo, alkyl, alkoxy or phenoxo. \(\text{R}_1\) and \(\text{R}_2\) independently of one another are each hydrogen or unsubstituted or substituted alkyl, \(\text{R}_3\) and \(\text{R}_4\) independently of one another are each hydrogen, halo, alkyl, alkoxy or unsubstituted or substituted amino. \(\text{Z}\) is a 5-or 6-membered aromatic heterocyclic ring or monoo- or poly-condensed aromatic carbocyclic ring, aliphatic group or one formed by combination thereof through a suitable bridging group, \(m\) and \(n\) independently of one another are each 0 or 1, provided that \(m+n\), and \(\epsilon\) is 1 or 2.

The present invention further provides a method for dyeing or printing fiber materials, which comprises using said asymmetric dioxazine compounds.

As to the symbols \(\text{A}_1\) and \(\text{A}_2\), the halo includes, for example, chloro and bromo, the alkoxy includes those of 1 to 4 carbon atoms such as methoxy and ethoxy, and the alkyl includes those of 1 to 4 carbon atoms such as methyl and ethyl. Among the groups represented by \(\text{A}_1\) and \(\text{A}_2\), sulfo is particularly preferable.

The unsubstituted or substituted alkyl represented by \(\text{R}_1\) and \(\text{R}_2\), includes those of 1 to 4 carbon atoms. Examples of the substituent of the alkyl are hydroxy, cyano, alkoxy, halo, carbamoyl, carboxy, \(\text{C}_1\text{-C}_4\) alkoxy carbonyl, \(\text{C}_1\text{-C}_4\) alkylcarboxyloxoy, sulfo and sulfamoyl.

Among the groups represented by \(\text{R}_1\) and \(\text{R}_2\), hydrogen is particularly preferable.

As examples of the halo, alkoxy and alkyl represented by \(\text{R}_3\) and \(\text{R}_4\), chloro and bromo, methoxy and ethoxy, and methyl and ethyl can be referred to, respectively.

Examples of the unsubstituted or substituted amino represented by \(\text{R}_3\) and \(\text{R}_4\), include \(\text{NH}_2\) and amino substituted once or twice by \(\text{C}_1\text{-C}_4\) alkyl.

As the group represented by \(\text{X}_1\) and \(\text{X}_2\), the halo is particularly preferable, among which chloro and bromo are most preferable.

As the unsubstituted or substituted aliphatic bridging groups represented by \(\text{W}\), \(\text{C}_2\text{-C}_4\) alkylene groups can be referred to, among which ethylene and propylene are particularly preferable.

As the unsubstituted or substituted aromatic bridging groups represented by \(\text{W}\), phenylene and naphthylene unsubstituted or substituted once, twice or three times by sulfo can be referred to, among which phenylene groups substituted once or twice by sulfo are particularly preferred.

In the present invention, the fiber-reactive group represented by \(\text{Z}\) is intended to mean those which can react under
dyeing or printing conditions with -OH, -NH- or -NH₂ group of the hydroxyl and/or amide group-containing materials to form a covalent bond.

As mentioned above, the fiber reactive group includes aromatic ones having at least one fiber reactive substituent on 5- or 6-membered aromatic heterocyclic ring or mono- or poly-condensed aromatic carbocyclic ring, aliphatic ones and those formed by combination thereof through a suitable bridging group. The heterocyclic ring includes, for example, monoazines, diazines and triazines such as pyridine, pyrimidine, pyridazine, pyrazine, thiazine, oxazine and asymmetric or symmetric triazine, and the carbocyclic ring includes, for example, quinoline, phthalazine, cinnoline, quinazoline, quinoxaline, acridine, phenazine and phenanthidine.

As the reactive substituent on the heterocyclic ring and the carbocyclic ring, halo (Cl, Br or F), ammoniums including hydrazinium, sulfonium, sulfonyl azide (-N₃), thiocyanato, thio, thioether, oxyether, sulfino and sulfo can be referred to.

As the heterocyclic ring type and carbocyclic ring type fiber-reactive group, the followings can be referred to:

2,4-difluorotriazin-6-yl,
2,4-dichlorotriazin-6-yl,
monohalo-s-triazinyl groups and particularly monochlorotriazinyl and monofluorotriazinyl groups substituted by alkyl, aryl, amino, monoalkylamino, dialkylamino, aralkylamino, arylamino, alkoxy, aryloxy, alkylthio or arylthio, such as:
2-amino-4-fluorotriazin-6-yl,
2-methylamino-4-fluorotriazin-6-yl,
2-ethylamino-4-fluorotriazin-6-yl,
2-isopropylamino-4-fluorotriazin-6-yl,
2-dimethylamino-4-fluorotriazin-6-yl,
2-diethylamino-4-fluorotriazin-6-yl,
2-[β-methoxyethylamino]-4-fluorotriazin-6-yl,
2-[β-hydroxyethylamino]-4-fluorotriazin-6-yl,
2-di([β-hydroxyethylamino]-4-fluorotriazin-6-yl,
2-[β-sulfoethylamino]-4-fluorotriazin-6-yl,
2-[β-sulforethylamino]-4-fluorotriazin-6-yl,
2-carboxymethylamino-4-fluorotriazin-6-yl,
2-di(carboxymethylamino)-4-fluorotriazin-6-yl,
2-sulfonemethyl-methylamino-4-fluorotriazin-6-yl,
2-[β-cyanoethylamino]-4-fluorotriazin-6-yl,
2-benzylamino-4-fluorotriazin-6-yl,
2-[β-phenylethylamino]-4-fluorotriazin-6-yl,
2-benzylethylamino-4-fluorotriazin-6-yl,
2-(4'-sulfinobenzyl)-amino-4-fluorotriazin-6-yl,
2-cyclohexylamino-4-fluorotriazin-6-yl,
2-(o-, m-, p-methylphenyl)-amino-4-fluorotriazin-6-yl,
2-(o-, m-, p-sulfo phenyl)-amino-4-fluorotriazin-6-yl,
2-(2‘,5’-disulfonyl)-amino-4-fluorotriazin-6-yl,
2-(o-, m-, p-chlorophenyl)-amino-4-fluorotriazin-6-yl,
2-(o-, m-, p-methoxyphenyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-methyl-4’-sulfonyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-methyl-5’-sulfonyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-chloro-4’-sulfonyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-chloro-5’-sulfonyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-methoxy-4’-sulfonyl)-amino-4-fluorotriazin-6-yl,
2-(o-, m-, p-carboxyphenyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-4’-disulfophenyl)-amino-4-fluorotriazin-6-yl,
2-(3‘,5’-disulfonyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-carboxy-4’-sulfonyl)-amino-4-fluorotriazin-6-yl,
2-(2‘-carboxy-5’-sulfonyl)-amino-4-fluorotriazin-6-yl,
2-(6’sulfonylphényl-2‘-yl)-amino-4-fluorotriazin-6-yl,
2-(4‘,8’-disulfonaphth-2‘-yl)-amino-4-fluorotriazin-6-yl,
2-(6’-sulfonaphth-2‘-yl)-amino-4-fluorotriazin-6-yl,
2-(N-methylphenyl)-amino-4-fluorotriazin-6-yl,
2-(N-ethylphenyl)-amino-4-fluorotriazin-6-yl,
2-(N-[β-hydroxyethylphenyl]-amino-4-fluorotriazin-6-yl,
the corresponding 4-chloro- and 4-bromo-triazinyl groups; and the corresponding groups obtained by a halogen interchange using a tertiary base such as trimethylamine, triethylamine, dimethyl-β-hydroxyethylamine, triethanolamine, N,N-dimethylhydrazine, pyridine, picoline, nicotinic acid or isonicotinic acid or sulfonic acid salts, particularly benzene-sulfonic acid or hydrogen sulfites; and mono-, di- or tri-halopyrimidinyl groups such as:

2,4-dichloropyrimidin-6-yl,
2,3,5-trichloropyrimidin-6-yl,
2,4-dichloro-5-nitro- or -5-methyl- or -5-carboxymethyl- or -5-carboxy- or -5-cyano- or -5-vinyl- or -5-sulfo- or -5-mono-, di- or tri-chloromethyll- or -5-carboxalkoxy-pyrimidin-6-yl,
2,6-dichloropyrimidine-4-carbonyl,
2,4-dichloropyrimidine-5-carbonyl,
2-chloro-4-methylpyrimidine-5-carbonyl, 2-methyl-4-chloropyrimidine-5-carbonyl,
2-methylthio-4-fluoropyrimidine-5-carbonyl,
6-methyl-2,4-dichloropyrimidine-5-carbonyl,
2,4,6-trichloropyrimidine-5-carbonyl,
2,4-dichloropyrimidine-5-sulfonyle, or 2-chloroquinazoline-3-carbonyl,
2- or 3-monochloroquinazoline-6-carbonyl,
2- or 3-monochloroquinazoline-6-sulfonyle,
2,3-dichloroquinazoline-6-carbonyl,
2,3-dichloroquinazoline-6-sulfonyle,
1,4-dichloroquinazoline-6-sulfonyle or -6-carbonyl,
2,4-dichloroquinazoline-7- or -6-sulfonyle or -6-carbonyl.
2- or 3- or 4- or 4'-5'-dichloropyridaz-6'-on-1'-yl)-phenylsulfonyle or -carbonyl, β-(4'-5'-dichloropyridaz-6'-on-1'-yl)-ethylcarbonyl,
N-methyl-(2,3-dichloroquinazoline-6-sulfonyle)-aminoacetyl,
N-methyl-N-(2,3-dichloroquinazoline-6-carbonyl)-aminoacetyl; and

the corresponding bromine and fluorine derivative of the above-mentioned chlorine-substituted heterocyclic groups, such as:

2-fluoro-4-pyrimidinyl,
2,6-difluoro-4-pyrimidinyl,
2,6-difluoro-5-chloro-4-pyrimidinyl,
2-fluoro-5,6-dichloro-4-pyrimidinyl,
2,6-difluoro-5-methyl-4-pyrimidinyl,
2-fluoro-5-methyl-6-chloro-4-pyridinyl,
2-fluoro-5-nitro-6-chloro-4-pyrimidinyl,
5-bromo-2-fluoro-4-pyrimidinyl,
2-fluoro-5-cyano-4-pyrimidinyl,
2-fluoro-5-methyl-4-pyrimidinyl,
2,5,6-trifluoro-4-pyrimidinyl,
5-chloro-6-chloromethyl-2-fluoro-4-pyrimidinyl,
5-chloro-6-dichloromethyl-2-fluoro-4-pyrimidinyl,
5-chloro-6-trichloromethyl-2-fluoro-4-pyrimidinyl,
5-chloro-2-chloromethyl-6-fluoro-4-pyrimidinyl,
5-chloro-2-dichloromethyl-6-fluoro-4-pyrimidinyl,
5-chloro-2-trichloromethyl-6-fluoro-4-pyrimidinyl,
5-chloro-2-fluorodichloromethyl-6-fluoro-4-pyrimidinyl,
2,6-difluoro-5-bromo-4-pyrimidinyl,
2-fluoro-5-bromo-6-methyl-4-pyrimidinyl,
2-fluoro-5-bromo-6-chloromethyl-4-pyrimidinyl,
2,6-difluoro-5-chloromethyl-4-pyrimidinyl,
2,6-difluoro-5-nitro-4-pyrimidinyl,
2-fluoro-6-methyl-4-pyrimidinyl,
2-fluoro-5-chloro-6-methyl-4-pyrimidinyl,
2-fluoro-5-chloro-4-pyrimidinyl,
2-fluoro-6-chloro-4-pyrimidinyl,
6-trifluoromethyl-5-chloro-2-fluoro-4-pyrimidinyl,
6-trifluoromethyl-2-fluoro-4-pyrimidinyl,
2-fluoro-5-nitro-4-pyrimidinyl,
2-fluoro-5-trifluoromethyl-4-pyrimidinyl,
2-fluoro-5-phenyl- or 5-methylsulfonylmethyl-4-pyrimidinyl,
2-fluoro-5-carboxamido-4-pyrimidinyl,
2-fluoro-5-carboxaminoxy-4-pyrimidinyl,
2-fluoro-5-bromo-6-trifluoromethyl-4-pyrimidinyl,
2-fluoro-6-carboxamido-4-pyrimidinyl,
2-fluoro-6-carboxaminoxy-4-pyrimidinyl,
2-fluoro-6-phenyl-4-pyrimidinyl,
2-fluoro-6-cyano-4-pyrimidinyl,
2-fluoro-4-dichloromethyl-5-chloropyrimidin-6-yl,
2-fluoro-5-chloropyrimidin-4-yl,
2-methyl-4-fluoro-5-methylsulfonylpyrimidin-6-yl,
2,6-difluoro-5-methylsulfonyl-4-pyrimidinyl,
2,6-dichloro-5-methylsulfonyl-4-pyrimidinyl,
2-fluoro-5-sulfonamido-4-pyrimidinyl,
2-fluoro-5-chloro-6-carboxaminoxy-4-pyrimidinyl,
2,6-difluoro-5-trifluoromethyl-4-pyrimidinyl; and

sulfonyl-containing triazine groups such as:

2,4-bis(phenylsulfonyl)-triazin-6-yl,
2-(3'-carboxyphenyl)-sulfonyl-4-chlorotriazin-6-yl,
2-(3'-sulphophenyl)-sulfonyl-4-chlorotriazin-6-yl,
2,4-bis(3'-carboxyphenylsulfonyl)-triazin-6-yl; and

sulfonyl-containing pyrimidine rings, such as:

2-carboxymethylsulfonyl-pyrimidin-4-yl,
2-methylsulfonyl-6-methylpyrimidin-4-yl,
2-methylsulfonyl-6-ethylpyrimidin-4-yl,
2-phenylsulfonyl-5-chloro-6-methyl-pyrimidin-4-yl,
2,6-bis-methylsulfonyl-pyrimidin-4-yl,
2,6-bis-methylsulfonyl-5-chloro-pyrimidin-4-yl,
2,4-bis-methylsulfonyl-pyrimidine-5-sulfonyl,
2-methylsulfonyl-pyrimidin-4-yl,
2-phenylsulfonyl-pyrimidin-4-yl,
2-trichloromethylsulfonyl-6-methyl-pyrimidin-4-yl,
2-methylsulfonyl-5-chloro-6-methyl-pyrimidin-4-yl,
2-methylsulfonyl-5-bromo-6-methyl-pyrimidin-4-yl,
2-methylsulfonyl-5-chloro-6-ethyl-pyrimidin-4-yl,
2-methylsulfonyl-5-chloro-6-chloromethylpyrimidin-4-yl,
2-methylsulfonyl-4-chloro-6-methylpyrimidine-5-sulfonyl,
2-methylsulfonyl-5-nitro-6-methyl/pyrimidin-4-yl,
2,5,6-tris-methylsulfonyl-pyrimidin-4-yl,
2-methylsulfonyl-5,6-dimethyl-pyrimidin-4-yl,
2-ethylsulfonyl-5-chloro-6-methyl-pyrimidin-4-yl,
2-methylsulfonyl-6-chloropyrimidin-4-yl,
2,6-bis-methylsulfonyl-5-chloro-pyrimidin-4-yl,
2-methylsulfonyl-6-carboxypyrimidin-4-yl,
2-methylsulfonyl-5-sulfopyrimidin-4-yl,
2-methylsulfonyl-6-carbamethoxy pyrimidin-4-yl,
2-methylsulfonyl-5-carboxypyrimidin-4-yl,
2-methylsulfonyl-5-cyano-6-methoxy pyrimidin-4-yl,
2-methylsulfonyl-5-chloropyrimidin-4-yl,
2-sulfoethylsulfonyl-6-methylpyrimidin-4-yl,
2-methylsulfonyl-5-bromopyrimidin-4-yl,
2-phenylsulfonyl-5-chloropyrimidin-4-yl,
2-carboxymethylsulfonyl-5-chloro-6-methylpyrimidin-4-yl,
2-methylsulfonyl-6-chloropyrimidine-4- or -5-carbonyl,
2,6-bis(methylsulfonyl)pyrimidine-4- or -5-carbonyl,
2-ethylsulfonyl-6-chloropyrimidine-5-sulfonyl,
2,4-bis(methylsulfonyl)pyrimidine-5-sulfonyl,
2-methylsulfonyl-4-chloro-6-methylpyrimidine-5-sulfonyl or -carbonyl,
2-chlorobenzothiazole-5- or -6-carbonyl or -5 or -6-sulfonyl,
2-arylsulfonyl or alkylsulfonylbenzothiazole-5- or -6-carbonyl or -sulfonyl, such as:
2-phenylsulfonylbenzothiazole-5- or -6-carbonyl or -5 or -6-sulfonyl, and
2-methylsulfonyl- or 2-ethylsulfonylbenzothiazole-5- or -6-sulfonyl or -5 or -6-carbonyl, and

the corresponding 2-sulfonylbenzothiazole-5- or -6-carbonyl or -sulfonyl derivatives having sulfo group in their fused benzene ring.

2-chlorobenzoxazole-5- or -6-carbonyl or -sulfonyl,
2-chlorobenzimidazole-5- or -6-carbonyl or -sulfonyl,
2-chloro-1-methylbenzimidazole-5- or -6-carbonyl or -sulfonyl,
2-chloro-4-methyl-1,3-thiazole-5-carbonyl or -4- or -5-sulfonyl and
4-chloro or 4-nitroquinoline-5-carbonyl N-oxide.

As examples of the aliphatic fiber-reactive group, the followings can be referred to:

acryloyl;
mono-, di- and tri-chloroacryloyls such as:
-CO-CH=CH-Cl,
-CO-CCI=CH_2,
-CO-CCI=CH-CH_2,
-CO-CCI=CH-COOH,
-CO-CH=CCl=COOH;
β-chloropropionyl,
3-phenylsulfonylpropionyl,
3-methylsulfonylpropionyl,
2-fluoro-2-chloro-3,3-difluorocyclobutane-1-carbonyl,
2,2,3,3-tetrafluorocyclobutane-1-carbonyl or -1-sulfonyl,

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β-(2,2,3,3-tetrafluorocyclobutyl)-aryloxy,
α- or β-bromoacyrloyl,
α- or β-alkyl- or aryl-sulfoacryloyl groups such as:
α- or β-methylsulfonylacryloyl,
chloroacetyl,
vinylsulfonyl and
-\(\text{SO}_2\text{CH}_2\text{CH}_2Z_1\) (\(Z_1\) represents a group eliminable by the action of alkali).

Preferable fiber-reactive groups represented by \(Z\) are those represented by the following formulas (II) to (IV):

\[
\begin{align*}
\text{II} & \quad \begin{array}{c}
\text{X}_3 \\
\text{X}_4
\end{array} \\
\text{III} & \quad \begin{array}{c}
\Phi \\
\text{R}_5 \text{R}_6 \text{R}_7
\end{array} \\
\text{IV} & \quad \begin{array}{c}
\Phi \\
\text{R}_8
\end{array}
\end{align*}
\]

wherein \(X_3\) and \(X_4\) independently represent chloro, fluoro,

\[
\begin{align*}
\text{R}_5 & \quad \begin{array}{c}
\Phi \\
\text{R}_6 \text{R}_7
\end{array} \\
\text{R}_8
\end{align*}
\]

(\(R_5, R_6\) and \(R_7\) represent optionally substituted alkyl group) or

(\(R_8\) is a hydrogen, cyano, carbamoyl, halo, carboxy, sulfo, hydroxy, vinyl or, unsubstituted or substituted alkyl group) and the mark * represents a bond linking to

\[
\begin{align*}
\text{IV} & \quad \begin{array}{c}
\Phi \\
\text{R}_2
\end{array} \\
\text{V} & \quad \begin{array}{c}
\text{R}_9 \\
\Phi
\end{array}
\end{align*}
\]

wherein \(B_1\) is an unsubstituted or substituted phenylene, alkylene or naphthylene group, \(R_9\) is hydrogen or an unsubstituted or substituted alkyl group, \(Z_1\) represents -\(\text{SO}_2\text{CH}_2\text{CH}_2\) or -\(\text{SO}_2\text{CH}_2\text{CH}_2Y_1\) (\(Y_1\) is a group capable of being split
by the action of an alkali), \( T \) represents halogen, alkoxy,

\[
\begin{align*}
-N \quad & \quad \text{R}_{10} \\
& \quad \text{R}_{11}
\end{align*}
\]

\( (\text{R}_{10} \text{ and R}_{11} \text{ independently of one another are each a hydrogen atom or unsubstituted or substituted alkyl, phenyl, naphthyl or benzyl group}), \)

\[
\begin{align*}
-\Theta \quad & \quad \text{R}_{5} \\
& \quad \text{R}_{6} \\
& \quad \text{R}_{7}
\end{align*}
\]

\( (\text{R}_{5}, \text{R}_{6} \text{ and R}_{7} \text{ are as defined above}), \)

\[
\begin{align*}
-\Theta \quad & \quad \text{R}_{8}
\end{align*}
\]

\( (\text{R}_{8} \text{ is as defined above) or} \)

\[
\begin{align*}
-N \quad & \quad \text{B}_{2} \quad \text{Z}_{2} \\
& \quad \text{R}_{12}
\end{align*}
\]

\( \text{[B}_{2} \text{ is an unsubstituted or substituted phenylene, alkyylene or naphthylene group, R}_{12} \text{ is a hydrogen atom or unsubstituted or substituted alkyl group and Z}_{2} \text{ is -SO}_{2}\text{CH} \text{=CH}_{2} \text{ or -SO}_{2}\text{CH}_{2}\text{CH}_{2} \text{Y}_{2} \text{ (Y}_{2} \text{ is a group capable of being split by the action of an alkali) and the mark * is as defined above;}} \)

\[
\begin{align*}
* & \quad \text{N} \quad \text{N} \quad \text{R}_{10} \\
& \quad \text{N} \quad \text{R}_{11} \\
& \quad \text{X}_{3}
\end{align*}
\]

\text{(IV)}

\[
\begin{align*}
\text{wherein X}_{3}, \text{ R}_{10}, \text{ R}_{11} \text{ and the mark * are as defined above.} \end{align*}
\]

\text{As the fiber-reactive group represented by Z, groups represented by the following formula (V) are particularly preferable from the viewpoint of dyeing performances:}
wherein B₂ is an unsubstituted or substituted phenylene, alkyne or naphthylene group, R₁₃ represents hydrogen or unsubstituted or substituted alkyl group and Z₃ represents -SO₂CH=CH₂ or -SO₂CH₂CH₂Y₃ (Y₃ is a group capable of being split by the action of an alkali) and T' represents chloro, fluoro, alkoxy.

(R₁₄ represents hydrogen or an unsubstituted or substituted alkyl group and R₁₅ represents hydrogen or an unsubstituted or substituted alkyl, phenyl or naphthyl group).

(B₄ represents an unsubstituted or substituted phenylene, alkyne or naphthylene group, R₁₆ is a hydrogen atom or, an unsubstituted or substituted alkyl group, Z₄ is -SO₂CH=CH₂ or -SO₂CH₂CH₂Y₄ (Y₄ is a group capable of being split by the action of an alkali) and the mark * is as defined above.

As examples of the unsubstituted or substituted alkyne group represented by B₁, B₂, B₃ and B₄, -(CH₂₂₅)²-, -CH₂₃₅⁻ and -(CH₂₉₂O(CH₂)₂₉- can be referred to. As said unsubstituted or substituted phenylene or naphthylene group, phenylene groups unsubstituted or substituted once or twice by substituent(s) selected from the group consisting of methyl.
ethyl, methoxy, ethoxy, chloro, bromo and sulfo, and naphthylene groups unsubstituted or substituted once by sulfo are preferable, of which concrete examples include the followings:
As examples of the alkyl or alkoxy group represented by X₁ and X₂, C₁-C₄ alkyl groups and C₁-C₄ alkoxy groups can be referred to.

As examples of the group capable of being split by the action of an alkali represented by Y₁, Y₂, Y₃, and Y₄, sulfuric ester group, thiosulfuric ester group, phosphoric ester group, acetic ester group and halogen can be referred to, among which sulfuric ester group is most preferable.

As examples of the unsubstituted or substituted alkyl group represented by R₉, R₁₂, R₁₃, and R₁₆, the followings can be referred to: a C₁-C₄ alkyl group such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl, 3-hydroxybutyl, 4-hydroxybutyl, 2,3-dihydroxypropyl, 3,4-dihydroxybutyl, cyanomethyl, 2-cyanoethyl, 3-cyanoethyl, methoxymethyl, ethoxymethyl, 2-methoxethyl, 2-ethoxyethyl, 3-methoxypropyl, 3-ethoxypropyl, 2-hydroxy-3-methoxypropyl, chloromethyl, bromomethyl, 2-chloroethyl, 2-bromoethyl, 3-chloropropyl, 3-bromopropyl, 4-chlorobutyl, 4-bromobutyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl, 1,2-dicarboxyethyl, carbamoylmethyl, 2-carbamoylethyl, 3-carbamoylpropyl, 4-carbamoylbutyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, 2-methoxycarbonylethyl, 2-ethoxycarbonylethyl, 3-methoxycarbonylpropyl, 3-ethoxycarbonylpropyl, 4-methoxycarbonylbutyl, 4-ethoxycarbonylbutyl, methylcarbonyloxymethyl, ethylcarbonyloxymethyl, 2-methyl-carbonyloxymethyl, 2-ethylcarbonyloxymethyl, 3-methylcarbonyloxymethyl, 3-ethylcarbonyloxymethyl, 4-methylcarbonyloxbutyl, 4-ethylcarbonyloxbutyl, sulfomethyl, 2-sulfooxyethyl, 3-sulfopropyl, 4-sulfobutyl, sulfamoylmethyl, 2-sulfamoylethyl, 3-sulfamoylpropyl and 4-sulfamoylbutyl. As R₉, R₁₂, R₁₃, and R₁₆, hydrogen, methyl and ethyl are particularly preferable.
As preferable examples of the unsubstituted or substituted alkyl group represented by \( R_{10}, R_{11}, R_{14} \) and \( R_{15} \), alkyl groups having 1 to 4 carbon atoms unsubstituted or substituted once or twice by a member selected from the group consisting of alkoxy groups having 1 to 4 carbon atoms, sulfo group, carboxy group, hydroxy group, chloro, phenyl group and sulfato group can be referred to.

Among them, particularly preferable are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, \( \beta \)-hydroxyethyl, \( \beta \)-sulfatoethyl, \( \beta \)-sulfoethyl, \( \beta \)-methoxymethyl and \( \beta \)-carboxyethyl.

As preferable examples of the unsubstituted or substituted phenyl group represented by \( R_{10}, R_{11} \) and \( R_{15} \), phenyl groups unsubstituted or substituted once or twice by a member selected from the group consisting of alkyl groups having 1 to 4 carbon atoms, alkoxy groups having 1 to 4 carbon atoms, sulfo group, carboxy group, chloro and bromo can be referred to.

Among them, phenyl, 2-, 3- or 4-sulphphenyl, 2,4- or 2,5-disulfonphenyl, 2-, 3- or 4-carboxyphenyl, 2-, 3- or 4-chlorophenyl, 2-, 3- or 4-methylphenyl and 2-, 3- or 4-methoxyphenyl are particularly preferable. As preferable examples of the unsubstituted or substituted naphthyl group represented by \( R_{10}, R_{11} \) and \( R_{15} \), naphthyl groups unsubstituted or substituted once, twice or three times by a member selected from the group consisting of hydroxy, carboxy, sulfo, alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms and chloro can be referred to.

Among them, particularly preferable are 2-, 3-, 4-, 5-, 6-, 7- or 8-sulfo-1-naphthyl, 1-, 5-, 6-, 7- or 8-sulfo-2-naphthyl, 1,5-, 5,7-, 5,6-, 4,8-, 4,7-, 3,8-, 4,6-, 3,7- or 3,6-disulfo-2-naphthyl, 4,6,8-, 2,4,7- or 3,8,6-trisulfo-1-naphthyl and 1,5,7-, 4,6,8- or 3,6,8-trisulfo-2-naphthyl.

As preferable examples of the unsubstituted or substituted benzyl represented by \( R_{10} \) and \( R_{11} \), benzyl groups unsubstituted or substituted once or twice by a member selected from the group consisting of alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, sulfo and chloro can be referred to.

Among them, benzyl and 2-, 3- or 4-sulfo benzyl are particularly preferable.

In the present invention, a case that either one of \( R_{10} \) and \( R_{11} \) is hydrogen, methyl or ethyl and the other of them is a phenyl group unsubstituted or substituted by \( C_1-C_4 \) alkyl, \( C_1-C_4 \) alkoxy, sulfo, carboxy or halogen or a \( C_1-C_4 \) alkyl group unsubstituted or substituted by alkoxy, sulfo, carboxy, hydroxy, chloro or sulfato and a case that \( R_{10} \) and \( R_{11} \) both are hydrogen groups are preferable from the viewpoint of dye characteristics. Regarding \( R_{14} \) and \( R_{15} \), too, the same combinations as in \( R_{10} \) and \( R_{11} \) are preferable from the viewpoint of dye characteristics.

As examples of compounds represented by \( HNR_{10}R_{11} \) and \( HNR_{14}R_{15} \) which can be used to form the groups

\[
\begin{align*}
- & N & R_{10} & \text{and} & - & N & R_{14} \\
& & R_{11} & & & & R_{15}
\end{align*}
\]

and respectively, in the above formulas (III), (IV) and (V) include the followings:

- ammonia;
- aromatic amines such as:

1-aminobenzene,
1-amino-2-, 3- or 4-methyl-benzene,
1-amino-3,4- or 3,5-dimethylbenzene,
1-amino-2-, 3- or 4-ethylbenzene,
1-amino-2-, 3- or 4-methoxybenzene,
1-amino-3,4- or 3,5-dimethylphenyl,
3- or 4-amino-phenylmethanesulfonic acid,
2-, 3- or 4-aminobenzensulfonic acid,
3-methylaminobenzensulfonic acid,
3-ethylaminobenzensulfonic acid,
4-methylaminobenzensulfonic acid,
4-ethylaminobenzensulfonic acid,
5-aminobenzene-1,3-disulfonic acid,
6-aminobenzene-1,3-disulfonic acid,
6-aminobenzene-1,4-disulfonic acid,
4-aminobenzene-1,2-disulfonic acid,
4-amino-5-methylbenzene-1,2-disulfonic acid,
2-, 3- or 4-aminobenzoic acid,
5-aminobenzene-1,3-dicarboxylic acid,
5-amino-2-hydroxybenzenesulfonic acid,
4-amino-2-hydroxybenzenesulfonic acid,
5-amino-2-ethoxybenzenesulfonic acid,
N-methyldiaminobenzene,
N-ethylaminobenzene,
1-methylamino-3- or -4-methylbenzene,
1-ethylamino-4-chlorobenzene,
1-ethylamino-3- or -4-methylbenzene,
1-(2-hydroxyethyl)-amino-3-methylbenzene,
3- or 4-methylaminobenzoic acid,
3- or 4-methylaminobenzenesulfonic acid,
2-aminonaphthalene-1-sulfonic acid,
4-aminonaphthalene-1-sulfonic acid,
5-aminonaphthalene-1-sulfonic acid,
6-aminonaphthalene-1-sulfonic acid,
7-aminonaphthalene-1-sulfonic acid,
8-aminonaphthalene-1-sulfonic acid,
1-aminonaphthalene-2-sulfonic acid,
4-aminonaphthalene-2-sulfonic acid,
5-aminonaphthalene-2-sulfonic acid,
6-aminonaphthalene-2-sulfonic acid,
7-aminonaphthalene-2-sulfonic acid,
7-methylaminonaphthalene-2-sulfonic acid,
7-ethylanaminonaphthalene-2-sulfonic acid,
7-butylnaminonaphthalene-2-sulfonic acid,
7-isobutylanaminonaphthalene-2-sulfonic acid,
8-aminonaphthalene-2-sulfonic acid,
4-aminonaphthalene-1,3-disulfonic acid,
5-aminonaphthalene-1,3-disulfonic acid,
6-aminonaphthalene-1,3-disulfonic acid,
7-aminonaphthalene-1,3-disulfonic acid,
8-aminonaphthalene-1,3-disulfonic acid,
2-aminonaphthalene-1,5-disulfonic acid,
3-aminonaphthalene-1,5-disulfonic acid,
4-aminonaphthalene-1,5-disulfonic acid,
4-aminonaphthalene-1,6-disulfonic acid,
8-aminonaphthalene-1,6-disulfonic acid,
4-aminonaphthalene-1,7-disulfonic acid,
3-aminonaphthalene-2,6-disulfonic acid,
4-aminonaphthalene-2,6-disulfonic acid,
3-aminonaphthalene-2,7-disulfonic acid,
4-aminonaphthalene-2,7-disulfonic acid,
6-aminonaphthalene-1,3,5-trisulfonic acid,
7-aminonaphthalene-1,3,5-trisulfonic acid,
4-aminonaphthalene-1,3,6-trisulfonic acid,
7-aminonaphthalene-1,3,6-trisulfonic acid,
8-aminonaphthalene-1,3,6-trisulfonic acid, and
4-aminonaphthalene-1,3,7-trisulfonic acid, and

aliphatic amines such as:
methyamine,
ethyamine,
n-propylamine,
isopropylamine,
n-butylamine,
iso-butylamine,
sec-butylamine, 
dimethylamine, 
diethylamine, 
methylethylamine, 
allylamine, 
2-chloroethylamine, 
2-methoxyethylamine, 
2-aminoethanol, 
2-methyaminoethanol, 

bis-(2-hydroxyethyl)amine, 
2-acetylaminoethyamine, 
1-amino-2-propanol, 
3-methoxypropylamine, 
1-amino-3-dimethylaminopropane, 
2-aminoethanesulfonic acid, 
aminomethanesulfonic acid, 
2-methylaminoethanesulfonic acid, 
3-amino-1-propanesulfonic acid, 
2-sulfatoethylamine, 
aminoacetic acid, 
methylaminoacetic acid, 
ε-aminocaproic acid, 
benzylamine, 
2-, 3- or 4-chlorobenzylamine, 
4-methylbenzylamine, 
N-methylbenzylamine, 
2-, 3- or 4-sulfobenzylamine, 
2-phenylethylamine, 
1-phenethylamine, and 
1-phenyl-2-propylamine.

Among them, particularly preferable are ammonia, ethylamine, taurine, N-methyltaurine, methylamine, n-propylamine, monoethanolamine, β-alanine, 2-chloroethylamine, 2-sulfatoethylamine, aniline, aniline-2-, -3- or -4-sulfonic acid, 2-, 3- or 4-carboxyamidine, N-methylenilene, N-ethylenilene, N-ethylenilene-2-, -3- or -4-chloroaniline, aniline-2, 4- or -2, 5-disulfonic acid, 2-, 3- or 4-chloroaniline, 2-, 3- or 4-methylaniline and 3- or 4-methyaminoethanesulfonic acid.

In the formulas (II), (III) and (IV), preferable examples of the unsubstituted or substituted alkyl group represented by R₁, R₂ and R₃ include alkyl groups such as alkyl; alkyl groups such as C₁-C₄ alkyl groups (for example, methyl, ethyl, propyl, butyl); and substituted C₁-C₄ alkyl groups, for example, such as hydroxyalkyl groups (for example, hydroxyethyl and hydroxypropyl), C₁-C₄ alkoxyalkyl groups (for example, methoxyethyl and ethoxyethyl), aryl-substituted alkyl groups (for example, benzyl, β-phenylethyl)], substituted amino alkyl groups (for example, β-dimethylaminoethyl, γ-dimethylaminopropyl, γ-diethylaminomethyl), and carboxyl alkyl groups (for example, carboxymethyl, carboxyethyl).

Among them, C₁-C₄ alkyl groups are preferable, and methyl group is particularly preferable.

As examples of the unsubstituted or substituted alkyl group represented by R₆, C₁-C₄ alkyl groups unsubstituted or substituted by hydroxy group and cyano group can be referred to.

As the group represented by R₇, hydrogen, carboxyl and carbamoyl are preferable, and carboxyl is particularly preferable.

Unless otherwise specified in the present invention, the alkyl and the alkoxy are those having 1 to 4 carbon atoms.
The compound of the present invention may be in the form of a free acid. Preferably, however, it is in the form of an alkali metal salt or an alkaline earth metal salt, for example, sodium salt and potassium salt.

The compound (I) of the present invention can be produced, for example, by allowing condensation reaction between an asymmetric dioxyzone intermediate represented by the following formula (VI):
wherein R1, R2, R3, R4, X1, X2, A1, A2, W, m, n and \( \ell \) are as defined above, and a compound represented by the following formula (VII):

\[
X-Z
\]  

(VII)

wherein X is a halo atom and Z is as defined above. The condensation reaction can be carried out in the presence of a de-hydrogen halide agent.

The asymmetric dioxazine intermediate represented by formula (VI) can be synthesized according to methods well known in themselves. For example, it can be synthesized in the following manner.

An asymmetric dianilide compound represented by the following formula (VIII):

\[
\begin{align*}
R_4 & & (\text{SO}_3\text{H}) \\
R_3 & & (\text{SO}_3\text{H}) \\
(A_1 \text{n}) & & (A_2 \text{m}) \\
(N & & N) \\
W & & W
\end{align*}
\]

(VIII)

wherein A1, A2, R1, R2, R3, R4, W, m, n and \( \ell \) are as defined above, is synthesized by a condensation reaction between a corresponding aniline compound and chloranil. Then, the asymmetric dianilide compound is cyclized, optionally in the presence of an oxidant, to form an asymmetric dioxazine intermediate of the formula (VI).

The compound of the present invention has a fiber-reactive group and can be used for dyeing or printing a hydroxy group- or carbonamide group-containing material. Preferably, the material to be dyed or printed is used in the form of a fiber material or a mixed woven material thereof.

Said hydroxy group-containing material includes natural and synthetic hydroxy group-containing materials such as cellulose fiber materials, their regenerated products and polyvinyl alcohol. As the cellulose fiber material, cotton and other plant fibers such as linen, flax, jute and ramie fibers are preferable. As the regenerated cellulose fiber, viscose staple and filament viscose can be referred to.

Said carbonamide group-containing material includes synthetic and natural polyamides and polyurethanes. Particularly in the form of a fiber, it includes wool and other animal furs, silk, leather, polyamide-6,6, polyamide-6, polyamide-11 and polyamide-4.

The compound (I) of the present invention can be effectively used for dyeing or printing said materials, particularly those such as fiber materials in a manner depending on physical and chemical properties of the materials. The manner includes, for example, exhaustion dyeing, padding and printing methods.

For example, the exhaustion dyeing method can be carried out at a temperature not exceeding 100°C in the presence of a neutral salt such as sodium sulfate and sodium chloride, and an acid binding agent such as sodium carbonate, sodium tertiary phosphate, sodium hydroxide and sodium bicarbonate optionally together with dissolving
assistants, penetrants or level dyeing agents. The neutral salt which can be used for promoting the exhaustion of the dye may be added in portions, if desired.

The padding method can be carried out by padding the materials at room or elevated temperature, followed by drying and then steaming or dry-heating the padded materials to perform dye-fixation.

The printing can be carried out in a one-phase or two-phase manner. The one-phase printing may be conducted by printing the fiber materials with a printing paste containing an acid binding agent such as sodium bicarbonate, followed by steaming at a temperature of 100° to 160°C. The two-phase printing may be conducted by printing the fiber materials with a neutral or weakly acidic printing paste, and passing the materials through a hot alkaline bath containing an electrolyte or over-padding the materials with an alkaline padding liquor containing an electrolyte, followed by a steaming or dry-heating treatment.

For the preparation of the printing paste, a paste or emulsifier such as starch ether is used optionally together with a conventional printing assistant such as urea and/or a dispersant.

As examples of the acid binding agent suitable for fixing the compound of this invention onto cellulose fiber, water-soluble basic salts formed between an alkali metal or an alkaline earth metal and an inorganic or organic acid or a compound liberating alkali in a heated state can be referred to. Particularly alkali metal salts formed between an alkali metal hydroxide and an inorganic or organic acid of weak or medium strength are preferable, among which sodium salts and potassium salts are the most preferable. Examples of such acid binding agent include sodium hydroxide, potassium hydroxide, sodium bicarbonate, sodium carbonate, sodium formate, potassium carbonate, sodium primary, secondary and tertiary phosphates, sodium silicate and sodium trichloroacetate.

The dyeing of synthetic and natural polyamide and polyurethane fibers can be carried out by performing exhaustion in an acid or weak acid bath at a controlled pH value and then making the bath neutral or in some cases alkaline to perform fixation. The dyeing temperature ranges usually from 60° to 120°C. In order to achieve a level dyeing, there may be used a conventional level dyeing agent such as a condensation product between cyanoacetic chloride and 3 times by mole of aminobenzensulfonic acid or aminonaphthalenesulfonic acid or an addition product between stearylamine and ethylene oxide.

The compound of the present invention is characterized in that it exhibits excellent performances in dyeing and printing fiber materials. It is particularly useful for dyeing cellulose fiber materials, and gives a dyed product excellent in light fastness, perspiration-light fastness, wet fastnesses such as washing resistance, peroxide-washing resistance, perspiration resistance, acid hydrolysis resistance and alkali hydrolysis resistance, and particularly in chlorine fastness, abrasion fastness and iron fastness.

It is further characterized by excellency in build-up, level-dyeing and wash-off properties and high solubility as well as high exhaustion and fixation percentages. Moreover, it is characterized in that it is hardly affected by changes in dyeing temperature and dyeing bath ratio, so that a dyed product with a stable quality can be obtained.

Moreover, the compound of the present invention is characterized in that it is resistant to color change at the time of fixing treatment and resin treatment of dyed product and resistant to the change due to contact with basic substances during storage.

The present invention will be illustrated in more detail by way of the following examples, wherein parts and % are by weight.

Example 1

An asymmetric dioxazine intermediate (33.8 parts) represented by the following formula in the free acid form:

```
\[
\begin{align*}
\text{SO}_3\text{H} & \quad \text{SO}_3\text{H} & \quad \text{SO}_3\text{H} \\
\text{NH}_2 & \quad \text{N} & \quad \text{O}
\end{align*}
\]
```

\(\lambda_{\text{max}}: 623 \text{ nm in aqueous medium}\)
was added to water (200 parts). Cyanuric chloride (5.5 parts) was added, and the mixture was stirred at a pH value of 5-6 at a temperature of 10-20°C until the reaction was completed. Then, 1-aminobenzene-3-β-sulfatoethylsulfone (6.4 parts) was added and stirred at a pH value of 2-4 at a temperature of 30-50°C until the reaction was completed. Thus, an asymmetric dioxazine compound represented by the following formula in the free acid form was obtained.

![Chemical Structure](image)

(λ<sub>max</sub>: 627 nm in aqueous medium)

Example 2

Example 1 was repeated, except that the dioxazine intermediate and 1-aminobenzene-3-β-sulfatoethylsulfone used in Example 1 were replaced with the compounds shown in Column 2 and Column 3, respectively, of the following table to obtain the corresponding asymmetric dioxazine compounds. When used for dyeing, these compounds gave dyed products of which hues were as shown in Column 4 of the table.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
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Cont'd...

**EP 0 472 975 B1**
(Cont'd)

| 4 | \[
\begin{align*}
&\text{SO}_3\text{H} \quad \text{NH}_2 \\
&\text{CH}_3
\end{align*}
\]  \\
| 5 | "  \\
| 6 | \[
\begin{align*}
&\text{SO}_3\text{H} \quad \text{NH}_2 \\
&\text{SO}_3\text{H} \quad \text{Br} \\
&\text{SO}_3\text{H} \quad \text{NH}_2 \\
&\text{SO}_3\text{H} \quad \text{SO}_3\text{H}
\end{align*}
\]  \\

Blue

Greenish blue

- Cont'd -
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<td>NH$_2$OCH$_3$SO$_2$C$_2$H$_4$OSO$_3$H</td>
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(Cont'd)

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(Chemical structures and descriptions are not transcribed due to the nature of the content.)
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(Cont'd)
Example 3

1-Aminobenzene-2,5-disulfonic acid (25.3 parts) and cyanuric chloride (18.4 parts) were subjected to a condensation reaction in water medium at pH 3-5 at 0-20°C. To the reaction mixture was added the same dioxazine intermediate (11.2 parts) as used in Example 1, and the condensation reaction was further made to progress. After the reaction, 1-aminobenzene-3-[3]-sulfatoethylsulfone (28.1 parts) was added to perform a third condensation reaction. Thus, an asymmetric dioxazine compound represented by the following formula in the free acid form was obtained:

\[(\lambda_{\text{max}}: 629 \text{ nm in aqueous medium})\]

Example 4

The asymmetric dioxazine compound obtained in Example 1 (45.5 parts) was added to water (500 parts). After adding aniline (2.8 parts) thereto, a condensation reaction was carried out at pH 2-7 at 40-80°C to obtain an asymmetric dioxazine compound represented by the following formula in the free acid form:

\[(\lambda_{\text{max}}: 630 \text{ nm in aqueous medium})\]

Example 5

Example 4 can be repeated, except that the asymmetric dioxazine compound and aniline used in Example 4 are replaced with each of the 96 kinds of asymmetric dioxazine compounds obtained in Example 2 and each of the following 15 kinds of amines, respectively. Thus, corresponding asymmetric dioxazine compounds can be obtained.
Example 6

Example 3 can be repeated, except that the dioxazine intermediate and 1-aminobenzene-3-β-sulfatoethylsulfone used in Example 3 are replaced with the compounds shown in Column 2 and Column 3, respectively, of the table of Example 2, and the 1-aminobenzene-2,5-disulfonic acid used in Example 3 is replaced with each of the following 17 kinds of amines. Thus, corresponding asymmetric dioxazine compounds can be obtained.

(1) 1-Aminobenzene-2,5-disulfonic acid
(2) 1-Aminobenzene-2,4-disulfonic acid
(3) Orthanilic acid
(4) 1-Aminonaphthalene-6,8-trisulfonic acid
(5) 2-Aminonaphthalene-1,5-disulfonic acid
(6) 2-Aminonaphthalene-3,6,8-trisulfonic acid
(7) o-Aminobenzoic acid
(8) Ammonia
(9) Ethylamine
(10) β-Hydroxyethylamine
(11) β-Alanine
(12) Taurine
(13) N-Methyltaurine
(14) NH₂C₆H₄OC₆H₄SO₂C₆H₄OSO₃H
(15) NH₂C₆H₄OC₆H₄SO₂CH₂CH₂
(16) NH₂C₆H₄SO₂C₆H₄Cl
(17) NH₂C₆H₄SO₂C₆H₄OSO₃H.

Example 7

Example 3 can be repeated, except that the 1-aminobenzene-2,5-disulfonic acid used in Example 3 is replaced with an equimolar quantity of each of the amines (2)-(17) in Example 6. Thus, corresponding asymmetric dioxazine compounds can be obtained.

Example 8

Example 4 can be repeated, except that aniline used in Example 4 is replaced with an equimolar quantity of each of the amines (2)-(15) in Example 5. Thus, corresponding asymmetric dioxazine compounds can be obtained.

Example 9

Example 1 was repeated, except that cyanuric chloride used in Example 1 was replaced with an equimolar quantity of 2-methoxy-4,6-dichloro-s-triazine to obtain an asymmetric dioxazine compound represented by the following formula in the free acid form:
Example 10

An asymmetric dioxazine intermediate (33.8 parts) represented by the following formula in the free acid form:

\[(\lambda_{\text{max}}: 623 \text{ nm in aqueous medium})\]

was added to water (200 parts), to which was added cyanuric chloride (5.5 parts). The mixture was stirred at pH 5-6 at 10-20°C. After the reaction, the reaction mixture was salted out with sodium chloride to obtain an asymmetric dioxazine compound represented by the following formula in the free acid form:

\[(\lambda_{\text{max}}: 620 \text{ nm})\]

Example 11

Example 10 was repeated, except that the dioxazine intermediate and cyanuric chloride used in Example 10 were replaced with the compounds shown in Column 2 and Column 3, respectively, of the following table. Thus, corresponding asymmetric dioxazine compounds were obtained. When used for dyeing, these compounds gave dyed products
of which hues were as shown in Column 4 of the following table.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
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<td><img src="image3.png" alt="Chemical Structure" /></td>
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<td>3</td>
<td>&quot;</td>
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<td>9</td>
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Example 12

Example 1 was repeated, except that the dioxazine intermediate, cyanuric chloride and 1-aminobenzene-3-β-sulfatoethylsulfone used in Example 1 were replaced with the compounds shown in Column 2, Column 3 and Column 4, respectively, of the following table to obtain corresponding asymmetric dioxazine compounds. When used for dyeing, these compounds gave dyed products of which hues were as shown in Column 5 of the following table.
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| 50 | (Cont'd) | ![Chemical Structure 3] | ![
| 55 | ![Chemical Structure 4] | ![Chemical Structure 5] | ![

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41
Example 13

The asymmetric dioxazine compound obtained in Example 1 (45.5 parts) was added to water (500 parts). After adding 3-carboxypyridine (3.7 parts) thereto, a substitution reaction was carried out at pH 2-5 at 40-80°C. Thus, an asymmetric dioxazine compound represented by the following formula in the free acid form was obtained:

\[
\text{\centering}
\begin{array}{c}
\text{(max: 622 nm)}
\end{array}
\]

Example 14

Example 13 can be repeated, except that the asymmetric dioxazine compound and 3-carboxypyridine used in Example 13 are replaced with each of the asymmetric dioxazine compounds used in Example 13 each of the following 10 kinds of amines respectively. Thus, corresponding asymmetric dioxazine compounds can be obtained.

1. \( \text{\centering} \)
2. \( \text{\centering} \)
3. \( \text{\centering} \)
4. \( \text{\centering} \)
5. \( \text{\centering} \)
6. \( \text{\centering} \)
7. \( \text{\centering} \)
8. \( \text{\centering} \)
9. \( \text{\centering} \)
10. \( \text{\centering} \)
Example 15

An asymmetric dioxazine intermediate (33.7 parts) represented by the following formula in the free acid form:

was added to water (300 parts). After adding cyanuric chloride (5.5 parts) thereto, the mixture was stirred at pH 5-6 at 10-20°C until the reaction was completed. Then, monoethanolamine (1.8 parts) was added, and the resulting mixture was stirred at pH 7-8 at 20-50°C until the reaction was completed. Then, 3-carboxypryidine (3.7 parts) was added and the resulting mixture was stirred at pH 2-5 at 40-80°C to carry out a substitution reaction. Thus, an asymmetric dioxazine compound represented by the following formula in the free acid form was obtained:

Example 16

Example 15 was repeated, except that the dioxazine intermediate, monoethanolamine and 3-carboxypryidine used in Example 15 were replaced with the compounds shown in Column 2, Column 3 and Column 4, respectively, of the following table, to obtain corresponding asymmetric dioxazine compounds. When used for dyeing, these compounds gave dyed products of which hues were as shown in Column 5 of the following table.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
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<td>CO$_2$H</td>
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</tr>
</tbody>
</table>
Example 17

Example 2 can be repeated, except that cyanuric chloride used in Example 2 is replaced with an equimolar quantity of each of the following 5 kinds of triazine compounds. Thus, corresponding asymmetric dioxazine compounds can be obtained.

Dyeing Example 1

Each of the asymmetric dioxazine compounds obtained in Example 10 and Example 11 (0.1, 0.3 and 0.6 part portions of every compound) was dissolved into water (200 parts). After adding sodium sulfate (10 parts) and cotton (10 parts) thereto, the temperature was elevated to 50°C, sodium carbonate (4 parts) was added, and dyeing was carried out for one hour. By washing the dyed cotton with water, soaped, again washed with water and dried, there was obtained a blue-colored dyed product excellent in fastnesses, particularly chlorine fastness, and having an excellent build-up property.

Dyeing Example 2

Using each of the asymmetric dioxazine compounds obtained in Examples 1-4, 9 and Examples 13, 15-16 (0.1, 0.3 and 0.6 part portions of every compound), dyeing was carried out in the same manner as in Dyeing Example 1, except that the dyeing temperature was 60°C. As the result, blue colored dyed products similarly excellent in fastness properties and build-up property were obtained.

Dyeing Example 3

Using each of the asymmetric dioxazine compounds obtained in Example 12 (0.1, 0.3 and 0.6 part portions of every compound), dyeing was carried out in the same manner as in Dyeing Example 1, except that the dyeing tem-
perature was 80°C. As the result, blue colored dyed products similarly excellent in fastness properties and build-up property were obtained.

Dyeing Example 4

Using each of the asymmetric dioxazine compounds obtained in Examples 1-4, 9, 15-16, color pastes having the following composition were prepared:

<table>
<thead>
<tr>
<th>Asymmetric dioxazine compound</th>
<th>5 parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>5 parts</td>
</tr>
<tr>
<td>Sodium alginate (5%) stock paste</td>
<td>50 parts</td>
</tr>
<tr>
<td>Hot water</td>
<td>25 parts</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>2 parts</td>
</tr>
<tr>
<td>Balance</td>
<td>13 parts</td>
</tr>
</tbody>
</table>

A mercerized cotton broad cloth was printed with each color paste. After intermediate drying, it was steamed at 100°C for 5 minutes, washed with hot water, soaped, again washed with hot water and dried. The dyed products thus obtained were excellent in fastness properties, particularly chlorine fastness, and build-up property.

Claims

1. An asymmetric dioxazine compound represented by the following formula (I) in the free acid form:

   ![Chemical Structure](image)

   (I)

   wherein A₁ and A₂ independently of one another are each sulfo, halo, alkyl or alkoxy, W is an unsubstituted or substituted aliphatic or aromatic bridging group, X₁ and X₂ independently of one another are each hydrogen, halo, alkyl, alkoxy or phenoxy, R₁ and R₂ independently of one another are each hydrogen or unsubstituted or substituted alkyl, R₃ and R₄ independently of one another are each hydrogen, halo, alkyl, alkoxy or unsubstituted or substituted amino, Z is a 5- or 6-membered aromatic heterocyclic ring or mono- or poly-condensed aromatic carbocyclic ring, aliphatic group or one formed by combination thereof through a suitable bridging group, m and n independently of one another are each 0 or 1, provided that m + n, and ℓ is 1 or 2.

2. A compound according to Claim 1, wherein the fiber-reactive group represented by Z is either one group represented by the following formulas (II), (III) or (IV):

   ![Chemical Structure](image)

   (II)
EP 0 472 975 B1

wherein $X_3$ and $X_4$ are each independently chloro, fluoro,

\[ R_5 \]
\[ \Phi N \]
\[ R_6 \]
\[ R_7 \]

(R$_5$, R$_6$ and R$_7$ are each independently unsubstituted or substituted alkyl) or

\[ \Phi N \]
\[ \text{R}_8 \]

(R$_8$ is hydrogen, cyano, carbamoyl, halogen, carboxy, sulfo, hydroxy, vinyl or, unsubstituted or substituted alkyl) and the mark * is a bond linking to

\[ \text{N} \]
\[ \text{R}_2 \]

\[ \text{N} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{N} \]

(III)

wherein B$_1$ is an unsubstituted or substituted phenylene, alkylene or naphthylene group, R$_9$ is hydrogen or unsubstituted or substituted alkyl, Z$_1$ is -SO$_2$CH=CH$_2$ or -SO$_2$CH$_2$CH$_2$Y$_1$ (Y$_1$ is a group capable of being split by the action of an alkali), T is halo, alkoxy,

\[ \text{N} \]
\[ \text{R}_{10} \]
\[ \text{R}_{11} \]

(R$_{10}$ and R$_{11}$ are each independently hydrogen or an unsubstituted or substituted alkyl, phenyl, naphthyl or benzyl group).
(R₅, R₆ and R₇ are as defined above).

(R₈ is as defined above) or

[B₂ is an unsubstituted or substituted phenylene, alkylene or naphthylene group, R₁₂ is hydrogen or unsubstituted or substituted alkyl and Z₂ is -SO₂CH=CH₂ or -SO₂CH₂CH₂Y₂ (Y₂ is a group capable of being split by the action of an alkali) and the mark * is as defined above;]

wherein X₃, R₁₀, R₁₁ and the mark * are as defined above.

3. A compound according to Claim 1, wherein the fiber-reactive group represented by Z is a group represented by the following formula (V):

wherein B₃ is an unsubstituted or substituted phenylene, alkylene or naphthylene group, R₁₃ is hydrogen or unsubstituted or substituted alkyl and Z₃ is -SO₂CH=CH₂ or -SO₂CH₂CH₂Y₃ (Y₃ is a group capable of being split by the action of an alkali) and T' is chloro, fluoro, alkoxy,
(R_{14} is hydrogen or unsubstituted or substituted alkyl and R_{15} is hydrogen or an unsubstituted or substituted alkyl, phenyl or naphthyl group).

(B_{4} is an unsubstituted or substituted phenylene, alkylene or naphthylene group. R_{16} is hydrogen or unsubstituted or substituted alkyl, Z_{4} is -SO_{2}CH=CH_{2} or -SO_{2}CH_{2}CH_{2}Y_{4} (Y_{4} is a group capable of being split by the action of an alkali); and the mark * represents a bond linking to

4. A compound according to any one of Claims 1 to 3, wherein X_{1} and X_{2} are each independently chloro or bromo.

5. A compound according to any one of Claims 1 to 4, wherein R_{3} and R_{5} are each independently hydrogen.

6. A compound according to any one of Claims 1 to 5, wherein W is phenylene substituted once or twice by sulfo, ethylene or propylene.

7. A compound according to any one of Claims 1 to 6, wherein A_{1} and A_{2} are each sulfo.

8. A compound according to any one of Claims 1 to 7, wherein either one of R_{3} and R_{4} is unsubstituted or substituted amino.
9. A compound according to any one of Claims 1 to 8, wherein W is phenylene substituted once or twice by sulfo.

10. A method for dyeing or printing a fiber material which comprises using the asymmetric dioxazine compound according to any one of Claims 1 to 9.

11. A process for producing an asymmetric dioxazine compound represented by the following formula (I) in the free acid form:

\[
\begin{align*}
\text{(I)} \\
R_3 & \quad (\text{SO}_3\text{H})\ell \\
N & \quad (A_1)_n \\
S & \quad \text{SO}_3\text{H} \\
X_1 & \quad \text{SO}_3\text{H} \\
N & \quad -W-N-Z \\
R_1 & \quad R_2 \\
(A_2)_m \\
\end{align*}
\]

wherein \(A_1\) and \(A_2\) independently of one another are each sulfo, halo, alkyl or alkoxy, W is an unsubstituted or substituted aliphatic or aromatic bridging group, \(X_1\) and \(X_2\) independently of one another are each hydrogen, halo, alkyl, alkoxy or phenoxy, \(R_1\) and \(R_2\) independently of one another are each hydrogen, halo, alkyl, alkoxy or unsubstituted or substituted amino, \(Z\) is a fiber-reactive group, \(m\) and \(n\) independently of one another are each 0 or 1, provided that \(m+n\), and \(\ell\) is 1 or 2, which comprises subjecting an asymmetric dioxazine intermediate represented by the following formula (VI):

\[
\begin{align*}
\text{(VI)} \\
R_3 & \quad (\text{SO}_3\text{H})\ell \\
N & \quad (A_1)_n \\
S & \quad \text{SO}_3\text{H} \\
X_1 & \quad \text{SO}_3\text{H} \\
N & \quad N-W-NH \\
R_1 & \quad R_2 \\
(A_2)_m \\
\end{align*}
\]

wherein \(R_1, R_2, R_3, R_4, X_1, X_2, A_1, A_2, W, m, n\) and \(\ell\) are as defined above, and a compound represented by the following formula (VII):

\[
\begin{align*}
X & \quad Z \\
\text{(VII)}
\end{align*}
\]

wherein \(X\) represents halogen atom and \(Z\) is as defined above, to a condensation reaction.

**Patentansprüche**

1. Asymmetrische Dioxazinverbindung, wiedergegeben durch die nachstehende Formel (I) in Form der freien Säure:
wobei $A_1$ und $A_2$, unabhängig voneinander, jeweils eine Sulfguppe, ein Halogenatom, einen Alkyl- oder Alkoxy-rest bedeuten, $W$ einen unsubstituierten oder substituierten aliphatischen oder aromatischen Brückenrest bedeutet, $X_1$ und $X_2$, unabhängig voneinander, jeweils ein Wasserstoffatom, ein Halogenatom, einen Alkyl-, Alkoxy- oder Phenoxysterrest bedeuten, $R_1$ und $R_2$, unabhängig voneinander, jeweils ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkylrest bedeuten, $R_3$ und $R_4$, unabhängig voneinander, jeweils ein Wasserstoffatom, ein Halogenatom, einen Alkyl-, Alkoxy- oder einen unsubstituierten oder substituierten Aminorest bedeuten, $Z$ einen 5- oder 6-gliedrigen aromatischen heterocyclischen Ring oder einen mono- oder poly kondensierten aromatischen carboxyclicen Ring, aliphatische Reste und Reste, die durch Kombination davon durch einen geeigneten Brückenrest erzeugt wurden, darstellt, $m$ und $n$, unabhängig voneinander, jeweils 0 oder 1 sind, mit der Maßgabe, daß $m$ # $n$ und $l$ 1 oder 2 ist.

2. Verbindung nach Anspruch 1, wobei die faserreaktive Gruppe, dargestellt durch $Z$, einen Rest, wiedergegeben durch die nachstehenden Formeln (II), (III) oder (IV), bedeutet:

wobei $X_3$ und $X_4$, jeweils unabhängig, ein Chloratom, Fluoratom.

(R$_5$, R$_6$ und R$_7$ bedeuten, jeweils unabhängig, einen unsubstituierten oder substituierten Alkylrest) oder

(R$_8$ bedeutet ein Wasserstoffatom, eine Cyano-, Carbamoylgruppe, ein Halogenatom, eine Carboxy-, Sulfo-, Hydroxy-, Vinylgruppe oder einen unsubstituierten oder substituierten Alkylrest) bedeuten und das Zeichen * eine Bindung, die an
bindet, bedeutet;

wobei B₁ einen unsubstituierten oder substituierten Phenyl-, Alkyl- oder Naphthylrest bedeutet, R₉ ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkylrest bedeutet, Z₁ -SO₂CH=CH₂ oder -SO₂CH₂CH₂Y₁ (Y₁ bedeutet einen Rest, der durch Einwirkung von Alkali abgespalten werden kann) ist, T ein Halogenatom, einen Alkoxyster;

(R₁₀ und R₁₁ bedeuten, jeweils unabhängig, ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkyl-, Phenyl-, Naphthyl- oder Benzylrest).

(R₅, R₆ und R₇ besitzen die vorstehend angegebenen Bedeutungen).

(R₈ besitzt die vorstehend angegebene Bedeutung) oder [B₂ bedeutet einen unsubstituierten oder substituierten Phenyl-, Alkyl- oder Naphthylrest, R₁₂ ist ein Wasserstoffatom oder ein unsubstituierter oder substituierter Alkylrest und Z₂ ist -SO₂CH=CH₂ oder -SO₂CH₂CH₂Y₂ (Y₂ bedeutet einen Rest, der durch Einwirkung von Alkali aufgespalten werden kann)] bedeutet und das Zeichen * die vorstehend angegebene Bedeutung besitzt;
wobei X₃, R₁₀, R₁₁ und das Zeichen * die vorstehend angegebene Bedeutung besitzt.

3. Verbindung nach Anspruch 1, wobei die faserrreaktive Gruppe, dargestellt durch Z, einen Rest, wiedergegeben durch die nachstehende Formel (V), bedeutet:

wobei B₃ einen unsubstituierten oder substituierten Phenylen-, Alkylen- oder Naphthylrest bedeutet. R₁₂ ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkylrest bedeutet und Z₂ -SO₂CH=CH₂ oder -SO₂CH₂CH₂Y₂ (Y₂ bedeutet einen Rest, der durch Einwirkung von Alkali abgespalten werden kann) ist und T' ein Chloratom, Fluoratom, einen Alkoxyrest,

(R₁₄ bedeutet ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkylrest und R₁₅ bedeutet ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkyl-, Pheny1- oder Naphthylrest).

oder
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\(-N-B_4-Z_4\)
\[\begin{array}{c}
\text{R}_{16}
\end{array}\]

(B\(_4\) bedeutet einen unsubstituierten oder substituierten Phenylen-, Alkylen- oder Naphthylenrest, R\(_{16}\) bedeutet ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkyrest. Z\(_4\) ist -SO\(_2\)CH\(_2\)- oder SO\(_2\)CH\(_2\)- oder \(Y_4\) bedeutet einen Rest, der durch Einwirkung von Alkali aufgespalten werden kann) bedeutet und das Zeichen 

\(-N-\)
\[\begin{array}{c}
\text{R}_2
\end{array}\]

verbindet.

4. Verbindung nach einem der Ansprüche 1 bis 3, wobei X\(_1\) und X\(_2\), jeweils unabhängig, ein Chlor- oder Bromatom bedeuten.

5. Verbindung nach einem der Ansprüche 1 bis 4, wobei R\(_1\) und R\(_2\), jeweils unabhängig, ein Wasserstoffatom bedeuten.

6. Verbindung nach einem der Ansprüche 1 bis 5, wobei W einen Phenylenrest bedeutet, der einfach oder zweifach durch die Sulfo-, Ethylen- oder Propylengruppe substituiert ist.

7. Verbindung nach einem der Ansprüche 1 bis 6, wobei A\(_1\) und A\(_2\), jeweils die Sulfguppe bedeuten.

8. Verbindung nach einem der Ansprüche 1 bis 7, wobei jeder der Reste R\(_3\) und R\(_4\) einen unsubstituierten oder substituierten Aminorest bedeuten.

9. Verbindung nach einem der Ansprüche 1 bis 8, wobei W einen Phenylenrest bedeutet, der einfach oder zweifach durch die Sulfguppe substituiert ist.


11. Verfahren zur Herstellung einer asymmetrischen Dioxazinverbindung, wiedergegeben durch die nachstehende Formel (I) in Form der freien Säure:

\[
\begin{array}{c}
\text{R}_3
\end{array} \quad (A_1)_n \quad (SO_3H)_n \quad \text{N} \quad \text{X}_1 \quad \text{O} \quad \text{SO}_3H
\]

\[
\begin{array}{c}
\text{R}_1 \quad \text{R}_2
\end{array}
\]

wobei A\(_1\) und A\(_2\), unabhängig voneinander, jeweils eine Sulfguppe, ein Halogenatom, einen Alkyl- oder Alkoxyrest bedeuten, W ein unsubstituiert oder substituierter aliphatischer oder aromatischer Brückenrest ist, X\(_1\) und X\(_2\), unabhängig voneinander, jeweils ein Wasserstoffatom, ein Halogenatom, einen Alkyl-, Alkoxy- oder Phenoxy-
rest bedeuten, $R_1$ und $R_2$, unabhängig voneinander, jeweils ein Wasserstoffatom oder einen unsubstituierten oder substituierten Alkylrest bedeuten, $R_3$ und $R_4$, unabhängig voneinander, jeweils ein Wasserstoffatom, ein Halogenatom, einen Alkyl- Alkoxy- oder einen unsubstituierten oder substituierten Aminrest bedeuten, $Z$ eine faserreaktive Gruppe bedeutet, $m$ und $n$, unabhängig voneinander, jeweils 0 oder 1 sind, mit der Maßgabe, daß $m \neq n$ und $1 \leq n \leq 2$ ist, umfassend die Kondensationsreaktion eines asymmetrischen Dioxazinzwischensprodukts, wiedergegeben durch die nachstehende Formel (VI):

![Chemical Structure](image)

(VI)

wobei $R_1, R_3, R_4, X_1, X_2, A_1, A_2, W, m, n$ und I die vorstehend angegebenen Bedeutungen besitzen, mit einer Verbindung, wiedergegeben durch die nachstehende Formel (VII):

![Chemical Structure](image)

(VII)

wobei X ein Halogenatom bedeutet und Z die vorstehend angegebene Bedeutung besitzt.

**Revisions**

1. Dérivé de dioxazine asymétrique représenté par la formule suivante (I) sous forme acide libre :

![Chemical Structure](image)

(I)

dans laquelle $A_1$ et $A_2$ indépendamment l'un de l'autre sont chacun un radical sulfo, halogéno, alkyle ou alcoxy. $W$ est un groupement de pontage aliphatique ou aromatique, non substitué ou substitué, $X_1$ et $X_2$ indépendamment l'un de l'autre sont chacun un atome d'hydrogène ou d'halogène ou un groupement alkyle, alcoxy ou phénoxy. $R_1$ et $R_2$ indépendamment l'un de l'autre sont chacun un atome d'hydrogène ou un groupement alkyle non substitué ou substitué, $R_3$ et $R_4$ indépendamment l'un de l'autre sont chacun un atome d'hydrogène ou d'halogène ou un groupement alkyle, alcoxy ou amino non substitué ou substitué. $Z$ est un noyau hétérocyclique aromatique à 5 ou 6 chaînons ou un noyau carbocyclique aromatique mono-ou polycyclique, un groupement aliphatique ou un groupement formé par leur combinaison par un groupement de pontage approprié, $m$ et $n$ indépendamment l'un de l'autre sont chacun 0 ou 1, pourvu que $m \neq n$, et I est 1 ou 2.

2. Composé selon la revendication 1, dans lequel le groupement réactif vis à vis des fibres représenté par $Z$ est soit un groupement représenté par les formules suivantes (II), (III) ou (IV):
dans laquelle $X_3$ et $X_4$ sont chacun indépendamment un radical chloro, fluoro,

(R$_5$, R$_6$ et R$_7$ sont chacun indépendamment un groupement alkyle non substitué ou substitué) ou

(R$_8$ est un atome d'hydrrogène ou un radical cyano, carbamoyle, halogéno, carboxy, sulfo, hydroxy, vinylique ou alkyle non substitué ou substitué)

et le repère * désigne une liaison liant

dans laquelle $B_1$ est un groupement phénylène, alkylène ou naphtylène non substitué ou substitué, R$_9$ est un atome d'hydrrogène ou un groupement alkyle non substitué ou substitué, Z$_1$ est $-SO_2CH=CH_2$ ou $-SO_2CH_2CH_2Y_1$ (Y$_1$ est un groupement pouvant être éliminé sous l'action d'une base), T est un radical halogéno, alcoxy.

(R$_{10}$ et R$_{11}$ sont chacun indépendamment un atome d'hydrrogène ou un groupement alkyle non substitué ou substitué, phénylène, naphtyle ou benzyle),
(R₅, R₆ et R₇ sont tels que définis précédemment),

(R₈ est tel que défini précédemment) ou

(N-B₂-Z₂)

[B₂ est un groupement phénylène, alkylène ou naphtylène non substitué ou substitué, R₁₂ est un atome d'hydrogène ou un groupement alkyle non substitué ou substitué et Z₂ est -SO₂CH=CH₂ ou -SO₂CH₂CH₂Y₂ (Y₂ est un groupement pouvant être éliminé sous l'action d'une base)) et le repère * est tel que défini précédemment;

dans laquelle X₃, R₁₀, R₁₁ et le repère * sont tels que définis précédemment.

3. Composé selon la revendication 1, dans lequel le groupement réactif vis à vis des fibres représenté par Z est un groupement représenté par la formule suivante (V):

dans laquelle B₂ est un groupement phénylène, alkylène ou naphtylène non substitué ou substitué, R₁₃ est un atome d'hydrogène ou un groupement alkyle non substitué ou substitué, et Z₃ est -SO₂CH=CH₂ ou -SO₂CH₂CH₂Y₃ (Y₃ est un groupement pouvant être éliminé sous l'action d'une base) et T est un radical chloro, fluoro, alcoxy.
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\[ \text{R}_{14} \quad \text{CONH}_2 \]

\[ \text{R}_{15} \quad \text{CO}_2\text{H} \]

ou

\[ \text{N-B}_4\text{-Z}_4 \]

\[ \text{R}_{16} \]

(B\(_4\) est un groupement phénylène, alkylène ou naphtylène non substitué ou substitué, R\(_{16}\) est un atome d'hydrogène ou un groupement alkyle non substitué ou substitué, Z\(_4\) est un groupement \(-\text{SO}_2\text{CH}^{-}\text{CH}_2\text{ ou } -\text{SO}_2\text{CH}_2\text{CH}_2\text{Y}_4\) (Y\(_4\) est un groupement pouvant être éliminé sous l'action d'une base) ; et le repère * représente une liaison liant à

\[ \text{N} \quad \text{R}_2 \]

4. Composé selon l'une quelconque des revendications 1 à 3, dans lequel X\(_1\) et X\(_2\) sont chacun indépendamment un atome de chlore ou de brome.

5. Composé selon l'une quelconque des revendications 1 à 4, dans lequel R\(_1\) et R\(_2\) sont chacun indépendamment un atome d'hydrogène.

6. Composé selon l'une quelconque des revendications 1 à 5, dans lequel W est un groupement phénylène substitué une ou deux fois par un radical sulfo, éthylène ou propylène.

7. Composé selon l'une quelconque des revendications 1 à 6, dans lequel A\(_1\) et A\(_2\) sont chacun un groupement sulfo.
8. Composé selon l'une quelconque des revendications 1 à 7, dans lequel l'un ou l'autre de R₃ et R₄ est un groupement amino non substitué ou substitué.

9. Composé selon l'une quelconque des revendications 1 à 8, dans lequel W est un groupement phényléne substitué une ou deux fois par des groupements sulfo.

10. Procédé pour teindre ou imprimer un matériau fibreux, qui consiste à utiliser le dérivé de dioxazine asymétrique selon l'une quelconque des revendications 1 à 9.

11. Procédé de production d'un dérivé de dioxazine asymétrique représenté par la formule suivante (I) sous forme acide libre :

\[
\text{(I)}
\]

dans laquelle A₁ et A₂ indépendamment l'un de l'autre sont chacun un radical sufo, halogéno, alkyle ou alcoxy. W est un groupement de pontage alaphatique ou aromatique, non substitué ou substitué. \(X₁\) et \(X₂\) indépendamment l'un de l'autre sont chacun un atome d'hydrogène ou d'halogène ou un groupement alkyle, alcoxy ou phénol. \(R₁\) et \(R₂\) indépendamment l'un de l'autre sont chacun un atome d'hydrogène ou un groupement alkyle non substitué ou substitué. \(R₃\) et \(R₄\) indépendamment l'un de l'autre sont chacun un atome d'hydrogène ou d'halogène ou un groupement alkyle, alcoxy ou amino non substitué ou substitué. Z est un groupement réactif vis à vis des fibres. m et n indépendamment l'un de l'autre sont chacun 0 ou 1, pourvu que \(m \neq n\), et 1 est 1 ou 2. procédé qui consiste à soumettre à une réaction de condensation un intermédiaire de dioxazine asymétrique représenté par la formule suivante (VI):

\[
\text{(VI)}
\]

dans laquelle \(R₁\), \(R₂\), \(R₃\), \(R₄\), \(X₁\), \(X₂\), \(A₁\), \(A₂\), W, m, n et l sont tels que définis précédemment, et un composé représenté par la formule suivante (VII):

\[
X·Z
\]

(VII)

dans laquelle X représente un atome d'halogène et Z est tel que défini précédemment.