Title: BLACK DICHROIC DYE

Abstract: Described is a black dichroic dye composition comprising 2 or more dyes, wherein at least one dye, generally a red dye and optionally a yellow dye, conforms to the formula A and at least one dye, usually a blue dye, conforms to the formula B. The dye composition is well suited for combination with liquid crystal material for use, inter alia, as polarizing film and/or in liquid crystal displays, showing, inter alia, high dichroic ratio and excellent compatibility with the LC material.
Black Dichroic Dye

The present invention relates to a black dichroic dye composition and its use in display technology, and to certain novel blue dyes for this purpose.

With the rapid development of displays based on liquid crystal (LC) technology over the last years dichroic dyes gain more and more interest for many different applications in this field like, e.g.:

Guest-host LC materials such as polymer dispersed, or polymer network dispersed LC materials (PDLC or PNLC) for
- Contrast enhancement films
- Reflective displays
- etc.

Using polymerizable LC materials (for example, LC molecules containing one or two alkyl(oxy) acrylate groups on one or both ends, such as compounds of the formula

\[
\text{Alkyl-0-[LC]-0-(CH}_2\text{)}_n\text{-O-C(R)=CH}_2,\]

wherein [LC] stands for the mesogenic part of the molecule, Alkyl is an alkyl group e.g. of 1 to 12 carbon atoms, R is H or methyl, n ranges from 1 to 12); these applications often include anisotropic films for
- (In-cell) polarizers
- Color correction films
- Brightness enhancement films (BEF)
- etc.

As it is well known in the art, addition of dyes to the LC in the liquid crystal display (LCD) leads to polarizer-free LCDs (so-called guest-host LCD system already noted above).

Suitable black mixtures of dichroic dyes (e.g. yellow, red, blue) are of special interest.

Today most polarizers for LCDs are based on uniaxially stretched polyvinylalcohol (PVA) films impregnated with iodine or dichroic colorants. Corresponding dichroic colorants must be compatible with PVA. Thus, they bear solubilizing substituents like e.g. sulfo groups. Such polarizer films usually cannot be used inside of a LC cell, whereas coatable materials based on a polymerizable liquid crystal are suited for this application. Corresponding dichroic dyes have to be compatible (high solubility) with the liquid crystal material, so dyes with e.g. sulfo groups cannot be applied for this type of polarizers.

Especially good solubility of the dichroic dyes in the LC medium, without negative influence on the order parameter of the LC, is a big challenge.

Known dichroic black dye mixtures for the applications mentioned above (see, for example, US-4565424) are of limited color strength. In consequence, a relatively high concentration of these
dye mixtures has to be applied for a black with good saturation. Such a high concentration can disturb the orientation of the liquid crystalline phase.

WO 201 1/024891 A 1 discloses a dichroic dye composition containing at least one dye of formula $A_{n}=N-A_{2}-L^{1}-A_{3}-L^{2}-A_{4}$, wherein $L^{1}$ and $L^{2}$ are each an azo, ester, imino or vinylen group, with the proviso that $L^{1}$ and $L^{2}$ are not both azo groups. Further, said composition may contain a thietyl-substituted dis- or trisazo dye. WO 201 1/024892 A 1 discloses a dichroic dye composition containing a thietyl-substituted dis- or trisazo dye.

Certain dyes have now been found, which provide a black with high color strength, high saturation, and good dichroic ratio and general properties.

In addition, some new blue dichroic dyes have been found with high dichroic ratio. These are very well suited as components for the present dichroic black mixtures.

The invention thus primarily pertains to a composition comprising 2 or more dyes, wherein at least one dye conforms to the formula A

\[
\begin{align*}
\text{(A)}
\end{align*}
\]

and at least one dye conforms to the formula B

\[
\begin{align*}
A_{n}=N-[A_{2}-N=N-]_{q}A_{3}-N=N-A_{4}
\end{align*}
\]

wherein

- each of $n, m, p$ is a number from 0 to 2;
- $q$ is 0 or 1;
- $A_{n}$ is a residue of one of the formulae

\[
\begin{align*}
\text{(B)}
\end{align*}
\]

$A_{2}$ is 1,4-phenylene, 1,4-phenylene substituted by one or two residues $R_{s}$, or is 1,4-naphthylene;

$A_{3}$ is 1,4-phenylene, 1,4-phenylene substituted by one or two residues $R_{s}$, or is 1,4-naphthylene;

$A_{4}$ is naphthyl substituted by one or two residues $d$-$C_{alkyl}$amino or di($C_{alkyl}$amino)amino whose alkyl groups are linked together to form one common bridging group

\[
\begin{align*}
\text{(C)}
\end{align*}
\]
d-Csalkylene or C2-C8alkylene interrupted by O, S and/or NR3, or by two residues Ci-Csalkylamino whose alkyl groups are linked together to form one common bridging group Ci-Csalkylene or C2-Csalkylene interrupted by O, S and/or NR3; or Ar4 is thiophenyl substituted by R11 and optionally further substituted by d-Csalkyl or phenyl or halogen or CN, Ar4 especially conforming to the formula

\[ \text{Ri} \text{ is Ci-Csalkyl, C3-Ci2cycloalkyl, or C3-Cscycloalkyl interrupted by O or NR3', each of which alkyl or cycloalkyl is unsubstituted or substituted; } \]

R3 is H or is as defined for Ri;
or Ri and R3 together are C2-Ci2alkylene or C2-Csalkylene interrupted by O and/or NR3, each of which is unsubstituted or substituted, Ri and R3 thus forming, together with the nitrogen atom they are attached to, an aliphatic N-heterocyclic residue of 2 to 12 carbon atoms;

R'3 is H or C8alkyl;
each of the residues R4, R5 and R6, if present, are independently selected from unsubstituted or substituted Ci-C4alkyl, Ci-C4alkoxy, halogen, or CN;

X is selected from H, Hal, or COOR2;

Xb is Hal, COOR2, CN, phenyl, Re-substituted phenyl, C3-Ci2cycloalkyl, Ci-Ci2alkyl-cyclohexyl, Hal is CF3 or halogen, especially CF3 or fluoro;

R2 is unsubstituted or substituted Ci-Csalkyl;

Rs is Ci-Csalkyl, Ci-Csalkoxy, Ci-Ci2alkyl-phenyl, Ci-Ci2alkyl-cyclohexyl, Ci-Ci2alkoxy-cyclohexyl, each of whose alkyl moieties are unsubstituted or substituted; or is C3-Ci2cycloalkyl, phenyl, CN, Hal;

R11 is NR"R", with R' and R" independently selected from H or Ci-C4alkyl or C3-Ci2cycloalkyl or phenyl or substituted phenyl; or R' and R" together forming one common bridging group Ci-Csalkylene or C2-Csalkylene interrupted by O, S and/or NR3; R11 especially being pyrrolidinyl or piperidinyl or di(Ci-C4alkyl)amino or morpholinyl;

R12 and R13 independently are H; Hal; nitro; formyl; SCN; CN; COOR2; COR2; Ci-Ci2alkyl; Ci-Ci2alkoxy; Ci-Ci2alkylthio; Ci-Ci2alkyl-SO2; phenyl; phenoxy; phenyl-SO2; phenyl or phenoxy or phenyl-SC"2 each of which is substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy or C3-Ci2alkylthio each of which is interrupted by O;

Ci-Csalkyl or C2-C3alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or COOR2 or phenyl or fluoro or CF3; or R12 and R13 together are C3-C4alkylene;

Ri4 is H; Hal; CN; SCN; COOR2; COR2; Ci-Ci2alkyl; C3-Ci2cycloalkyl Ci-Ci2alkoxy; Ci-Ci2alkylthio; Ci-Ci2alkylamino; di(Ci-Ci2alkyl)amino; pyrrolidinyl; piperidinyl; morpholinyl; phenyl; phenyl-SO2; phenyl substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy or C3-Ci2alkylthio each of which is interrupted by O;

Ci-Csalkyl or C2-C3alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or COOR2 or phenyl or fluoro or CF3; or R12 and R13 together are C3-C4alkylene;

Ri5 is H; Hal; OCF3; CN; COOR2; COR2; Ci-Ci2alkyl; Ci-Ci2alkoxy; Ci-Ci2alkylthio; Ci-Ci2alkylamino; di(Ci-Ci2alkyl)amino; Ci-Ci2alkyl-CON H; Ci-Ci2alkyl-SO2; pyrrolidinyl; di(Ci-Ci2alkyl)amino; morpholinyl; phenyl; phenyl-SO2; phenyl or phenyl-SO2 substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio or CN or CFs or OCF3; C2-Ci2alkyl or
c3-C2alkoxy or c3-C2alkylthio each of which is interrupted by O; d-Csalkyl or C2-C3alkenyl or 
Ci-Csalkoxy or Ci-i-Csalkylthio or Ci-C8alkyl-SO2 each of which is substituted by CN or COOR2 or 
or COR2 or phenyl or Re-substituted phenyl or fluoro or CF3;
R16 and R17 independently are H, halogen, nitro, Ci-C2alkyl, Ci-Csalkoxy;
where any substituent of alkyl moieties mentioned is preferably selected from halogen, CF3, CN, 
O H, Ci-C4alkyl, Ci-C4alkoxy, phenyl; C2-C8dialkylamino, or a N-bonded aliphatic or aromatic 
heterocyclic ring containing 2 to 5 carbon ring atoms and optionally one oxygen ring atom 
besides the bonding nitrogen atom.

10 Alkyl stands for any acyclic saturated monovalent hydrocarbyl group; alkenyl denotes such a 
group but containing at least one carbon-carbon double bond (such as in allyl). In case that an 
alkenyl group contains more than one double bond, these bonds usually are not cumulated, but 
may be arranged in an alternating order, such as in [CH=CH]n or [CH=C(CH3)]n, wherein n may be, for example, from the range 2-50. Where not defined otherwise, preferred alkyl 
contains 1-12 carbon atoms; preferred alkenyl contains 2-3 carbon atoms.

Where indicated as interrupted, any alkyl moiety of more than one, especially more than 2 
carbon atoms, or such alkyl or alkylene moieties which are part of another moiety, may be 
interrupted by a heterofunction such as O, S, COO, OCNR10, OCOO, OCONR10, NR10CNR10, or 
NR10 or NR3, where R3 is as defined above and R10 is, for example, H, Ci-C2alkyl, C3-
Ci2cycloalkyl, phenyl. They can be interrupted by one or more of these spacer groups, one 
group in each case being inserted, in general, into one carbon-carbon bond of the alkyl or 
alkylene moiety or a carbon-carbon bond the moiety is bonding to. Hetero-hetero bonds, for 
example O-O, S-S, NH-NH, etc., usually do not occur; if the interrupted alkyl is additionally 
substituted, the substituents are generally not a to the heteroatom; interrupted alkoxy or 
alkylthio contain interrupting heteroatoms within the carbon chain. If two or more interrupting 
groups of the type -O-, -NR10-, -S- occur in one radical, they often are identical. Examples for 
interrupted cycloalkyls are dioxanyl, morpholinyl, pyrrolidinyl, piperidinyl, piperazinyl.

30 Residues morpholinyl, piperidinyl, pyrrolidinyl are preferably N-bonded, i.e.

The term alkyl, whereever used, thus mainly embraces linear or branched, especially 
uninterrupted and, where appropriate, substituted Ci-C22alkyl such as methyl, ethyl, propyl, 
isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 
1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isooctyl, 1,1,3,3-tetramethylbutyl, 1-methyl-
heptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, 
nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethyloxy, tridecyl, 
tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl. Alkoxy is alkyl-O-; alkylthio is alkyl-S-.
The term alkenyl, wherever used, thus mainly embraces uninterrupted and, where appropriate,
substituted C2-C22alkyl such as vinyl, allyl, etc.

Cycloalkyl such as C3-Ci2cycloalkyl or said cycloalkyl substituted e.g. by one to three Ci-C4alkyl
groups includes cyclopropyl, cyclobutyl, cyclopentyl, methylvyclohexyl, dimethylcycloalkyl, cyclohexyl, methylvyclohexyl, dimethylcyclohexyl, trimethylcyclohexyl, tert-butylicyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloododecyl, 1-adamantyl, or 2-adamantyl. Cyclohexyl, 1-adamantyl and cyclopentyl are most preferred. C3-Ci2cycloalkyl includes
cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl,
cycloundecyl, cycloododecyl; preferred among these residues are C3-C6cycloalkyl as well as
cyclododecyl, especially cyclohexyl. Further ring structures occuring are heterocyclic aliphatic rings (heterocycloalkyl) usually containing 5 to 7 ring members, among them at least 1,
especially 1-3, heteromoieties, usually selected from O, S, NR'3, NR10, where R10 is as explained above for interrupting NR1o-groups; examples include C4-C8cycloalkyl, which is interrupted by S, O, or NR10, such as piperidyl, tetrahydrofuranyl, piperazinyl and morpholinyl;
examples for C2-C4heterocycloalkyl include oxiranyl, oxetanyl, piperazinyl, morpholinyl.
Unsaturated variants may be derived from these structures by abstraction of a hydrogen atom on 2 adjacent ring members with formation of a double bond between them; an example for such a moiety is cyclohexenyl.

Alkyoxy such as Ci-C24alkoxy is a straight-chain or branched radical, e.g. methoxy, ethoxy, n-
propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy or tert-amyloxy,
heptyloxy, octyloxy, isoctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy,
pentadecyloxy, hexadecyloxy, heptadecyloxy and octadecyloxy.

Ci-Ci2alkylthio radicals are straight-chain or branched alkylthio radicals, such as e.g. methylthio,
ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, pentylthio, isopentylthio, hexylthio,
heptylthio, octylthio, decylthio.

Naphthyl is in most cases 1-naphthyl; 1,4-naphthylene is the residue.

Halogen denotes I, Br, CI, F, preferably F, CI, Br, especially F.

Ar4 as naphthyl substituted by one or two residues d-Csalkylamino or d(Ci-C8alkyl)amino or
d(Ci-C8alkyl)amino whose alkyl groups are linked together to form one common bridging group
C-i-Csalkylene or C2-Csalkylene interrupted by O, S and/or NR3, or by two residues Ci-
Csalkylamino whose alkyl groups are linked together to form one common bridging group Ci-
Csalkylene or C2-Csalkylene interrupted by O, S and/or NR3, is preferably
with Rig being d-Csalkyl and R20 being H or C-i-Csalkyl, or R19 and R20 forming a common bridging group d-Csalkylene or C2-Csalkylene interrupted by O, S and/or NR3, especially O, e.g. pyrrolidinyl, piperidinyl or morpholinyl; or

with R18 and R19 being d-Csalkylamino whose alkyl groups form a common bridging group Ci-C3alkylene and R20 being H.

NR1R3, with R1 and R3 together forming, with the nitrogen atom they are attached to, an aliphatic heterocyclic residue of 2 to 12 carbon atoms, or a N-bonded aliphatic heterocyclic ring containing 2 to 12 carbon ring atoms and optionally interrupted by O, S and/or NR3, each of which is unsubstituted or substituted, is in preferred cases morpholinyl, piperidinyl, pyrrolidinyl or, where appropriate, a Ci-C4alkyl substituted variant thereof.

In a preferred aspect, the invention relates to a composition, wherein the at least one dye of formula A comprises a red dye and optionally a yellow dye, and the dye of formula B comprises a blue dye, which composition is a black dichroic dye composition.

Preferably, the invention relates to a composition comprising 3 or more dyes, wherein at least 2 dyes conform to the formula A

and at least one dye conforms to the formula B

wherein X, R1, R3, R4, R5, R6, n, m and p are defined as above.

In general, the black dichroic dye of the invention essentially consists of the dye of formulae A (usually one yellow and one red dye or only one red dye) and B (blue), i.e. no other dye is contained in amounts effective to significantly alter the color and/or the dichroic effect in the LC.
material. Accordingly, the dichroic dye of the invention is present in at least 90%, preferably 95% by weight, based on the total weight of the dichroic dyes.

In the dye compositions of the invention, the 2 dyes of formula A usually are a yellow dye and a red dye, and the dye of formula B is a blue dye, their mixture forming the black dichroic dye composition.

Compounds of the formula A often conform to the formula A1

\[
\begin{array}{c}
\begin{array}{c}
(R_4)\text{m} \\
X \\
N \\
(R_5)\text{n}
\end{array} \\
\begin{array}{c}
N \\
(R_1)\text{N} \\
N \\
(R_3)
\end{array}
\end{array}
\]

(A1)

wherein m is 0 or 1, R_4 and R_5, if present, are selected from C_i-C_4 alkyl, Hal is F or CF_3, and the other symbols are defined as above.

The optional yellow dye preferably conforms to formula A or A1 with the moiety \(-N(R_i)R_3\) being morpholinyl and any of R_4, R_5, R_6, if present, being methyl.

The red dye preferably conforms to formula A or A1 with the moiety \(-N(R_i)R_3\) being pyrrolidinyl or piperidinyl or di(C_i-C_4 alkyl)amino, and any of R_4, R_5, R_6, if present, being methyl.

The dye of formula B generally denotes the blue dye, which is preferably conforming to one of the formulae B_1, B_2, B_3, B_4

\[
\begin{array}{c}
\begin{array}{c}
X_b \\
N \\
N-Ar-N \\
N \\
R_4
\end{array} \\
\begin{array}{c}
N \\
N-Ar-N \\
N \\
R_18 \\
N \\
R_19 \\
N \\
R_20
\end{array}
\end{array}
\]

(B1)

\[
\begin{array}{c}
\begin{array}{c}
Ar_1 \\
N \\
N-Ar-N \\
N \\
R_16 \\
N \\
R_19 \\
N \\
R_20
\end{array}
\end{array}
\]

(B2)
wherein, in any of the formulae B1, B2, B3 and B4, q is 0 or 1;

Ar is 1,4-phenylene; 1,4-phenylene substituted by methyl; or is 1,4-naphthylene;
An is a residue of one of the formulae

Ar3 is 1,4-phenylene, 1,4-phenylene substituted by one or two methyl, or is 1,4-naphthylene;
Xb is Hal, COOR2, CN, phenyl, substituted phenyl, cyclohexyl, c±C2alkyl-cyclohexyl;

Hal is CF3 or fluoro;
R2 is c±C8alkyl;
R* is c±C8alkyl, cyclohexyl, c±C8alkyl-cyclohexyl;
R11 is pyrrolidinyl or piperidinyl or di(C1-C4alkyl)amino or morpholinyl;
R12 and R13 independently are H; Hal; CN; COOR2; c±C8alkyl; phenyl; phenyl substituted by phenyl or c±Csalkyl or cyclohexyl or c±Csalkoxy; C2-Csalkyl or c±Csalkythio each of which is interrupted by O; c±Csalkyl or vinyl each of which is substituted by CN or COOR2; or R12 and R13 together are C3-C4alkylene;
R14 is CF3; CN; COOR2; c±C8alkyl; c±C8alkoxy; c±C8alkylthio; pyrrolidinyl; di(C1-C4alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or c±Csalkyl; C2-Csalkyl interrupted by O; c±Csalkyl or vinyl or c±Csalkythio each of which is substituted by CN or COOR2 or phenyl or CF3;
R15 is CF3; OCF3; CN; COOR2; c±C8alkyl; c±C8alkoxy; c±C8alkylthio; c±C8alkyl-SO2; pyrrolidinyl; di(C1-C4alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or c±C8alkyl; C2-Csalkyl interrupted by O; c±Csalkyl or vinyl or c±Csalkythio or C1-C8alkyl-SO2 each of which is substituted by CN or COOR2 or phenyl or CF3;
R16 and R17 independently are H; halogen, nitro;
R18 is H or c±Csalkylamino;
R19 is c±Csalkyl;
R20 is H or c±Csalkyl;

or the alkyl groups of R* and R19 form a common bridging group c±C3alkylene;
and all other symbols are as defined further above.
Accordingly, a preferred composition is a composition, wherein the yellow dye conforms to
formula \( A \) or \( A_1 \) with the moiety \(-N(R_i)R_3\) being morpholinyl and any of \( R_4, R_5, R_6 \), if present, being methyl; and
the red dye conforms to formula \( A \) or \( A_1 \) with the moiety \(-N(R_i)R_3\) being pyrrolidinyl or piperidinyl or di(\(\text{C}_i-\text{C}_4\)alkyl)amino, and any of \( R_4, R_5, R_6 \), if present, being methyl; and
the dye of formula \( B \) is a blue dye conforming to one of the formulae \( B_1, B_2, B_3, B_4 \), as described herein-before.

A particularly preferred composition is a composition containing a compound \( A_2 \)

\[
\begin{align*}
\text{Hal} &- \text{N} - \text{N} - \text{N} - \text{N} - \text{O} \\
\text{(CH}_3\text{)}_n
\end{align*}
\]  

(A2)

and a compound \( A_3 \)

\[
\begin{align*}
\text{Hal} &- \text{N} - \text{N} - \text{N} - \text{N} - \text{N} \\
\text{(CH}_3\text{)}_n
\end{align*}
\]  

(A3)

and at least one of the compounds \( B_6, B_6', B_7, B_8, B_{10} \)

\[
\begin{align*}
\text{Hal} &- \text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \text{R}_{19} - \text{R}_{20} \\
\end{align*}
\]  

(B6)

\[
\begin{align*}
\text{Hal} &- \text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \text{R}_{19} - \text{R}_{20} \\
\end{align*}
\]  

(B6')

\[
\begin{align*}
\text{Hal} &- \text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \text{R}_{19} - \text{R}_{20} \\
\end{align*}
\]  

(B7)
wherein Hal is fluoro or CF3;
n is a number from 0 to 2;
Rig is branched C3-C6alkyl and R20 is H, or R19 and R20 are Ci-C4alkyl; and
R2 is linear or branched Ci-Csalkyl;
q is 0 or 1;
Ar is phenyl substituted by Xb, or is a heterocyclic residue of one of the formulae

Ar2 is 1,4-phenylene, 1,4-phenylene substituted by Ci-C4alkyl, or is 1,4-naphthylene;
Ar3 is 1,4-phenylene, 1,4-phenylene substituted by Ci-C4alkyl, or is 1,4-naphthylene;
Xb is Hal, COOR2, CN, phenyl, Re-substituted phenyl, C3-Ci2cycloalkyl, Ci-Ci2alkyl-cyclohexyl,
Ci-Ci2alkoxy-cyclohexyl;
Hal is CF3 or fluoro;
R2 is Ci-Ci2alkyl;
R5 is pyrrolidinyl or piperidinyl or di(Ci-C4alkyl)amino or morpholiny;
R12 and R13 independently are H, Hal, CN, COOR2, Ci-Csalkyl, Ci-Csalkoxy, Ci-Csalkylthio, phenyl; phenyl substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy C3-Ci2alkylthio each of which is interrupted by O; Ci-Cealkyl or C2-C3alkeny1 or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or
COOR2 or phenyl or fluoro or CF3; or R12 and R13 together are C3-C4alkylene;
Ri4 is H, CF3, CN, COOR2, Ci-Csalkyl, Ci-Csalkoxy, Ci-Csalkylthio, pyrrolidinyl, piperidinyl, di(Ci-C4alkyl)amino, morpholiny, phenyl; phenyl substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy C3-Ci2alkylthio each of which is interrupted by O; Ci-Csalkyl or C2-C3alkeny1 or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or
which is substituted by CN or COOR2 or phenyl or fluoro or CF3;
Ri5 is H, CF3, OCF3, CN, COOR2, Ci-Ci2alkyl, Ci-Ci2alkoxy, Ci-Ci2alkylthio, Ci-Ci2alkyl-S022; pyrrolidinyl; di(Ci-C4alkyl)amino, morpholiny, phenyl; phenyl substituted by phenyl or Ci-Csalkyl
or cyclohexyl or d-Csalkoxy or Ci-Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy or C3-Csalkylthio each of which is interrupted by O; Ci-Ci8alkyl or C2-C3alkenyl or Ci-Ci8alkoxy or Ci-Ci8alkylthio or Ci-Csalkyl-S02 each of which is substituted by CN or COOR2 or phenyl or fluoro or CF3; R16 and R17 independently are H, halogen, nitro, Ci-Ci2alkyl, Ci-Ci2alkoxy.

An example for a black dichroic dye mixture of the invention for the use in polarizing film of LC display is the combination of the 3 azo compounds A2a, A3a and one of B6a or B7a or B8a, as black dyestuff:

Another preferred composition is a composition, wherein one dye conforms to formula A4
wherein X is H, m is 1, n is 0, 1 or 2, 
R₄ and R₅ are methyl,
and the moiety -N(Rᵢ)ᵢR₃ is pyrrolidinyl;
and at least one compound of formulae B₁, B₂, B₃ or B₄ as defined above, preferably at least one of the compounds of formulae B₆, B₆', B₇, B₈, or B₁₀, more preferably a compound of formula B₁₀.

Another preferred blue dye for use in the black dichroic dye composition of the invention is the one of formula B₁₀, or more preferably of formula B₁₁, B₁₂, B₁₃, which formulae are explained below.

Among the dyes of formula B₁₀, preferred ones conform to formula B₁₁, B₁₂ and/or B₁₃

\[ \text{(B11)} \]

\[ \text{(B12)} \]

\[ \text{(B13)} \]

wherein
q is 0 or 1;
Ar₅ is a heterocyclic residue of the formula
Ar₆ is a heterocyclic residue of one of the formulae
and other symbols are as defined for formula B₁₀;
especially those wherein
Xb is Hal, COOR2, CN, phenyl, R8-substituted phenyl; Hal is CF3 or fluoro;
R2 is d-Cealkyl;
R3 is Ci-Csalkyl, cyclohexyl, phenyl, Ci-Csalkyl-phenyl, di(Ci-C4alkyl)amino;
R12 and R13 independently are H; Hal; CN; COOR2; Ci-Csalkyl; phenyl; phenyl substituted by
phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy; C2-Csalkyl or Cs-Csalkythio each of which is
interrupted by O; Ci-Csalkyl or vinyl each of which is substituted by CN or COOR2; or R12 and
R13 together are C3-C4alkylene;
R4 is CF3; CN; COOR2; d-Cealkyl; Ci-C8alkoxy; Ci-C8alkythio; pyrrolidinyl; di(Ci-
C4alkyl)amino; morpholinyl; phenyl substituted by phenyl or Ci-Csalkyl; C2-Csalkyl
interrupted by O; Ci-Csalkyl or vinyl or Ci-Csalkythio each of which is substituted by CN or
COOR2 or phenyl or CF3;
R5 is CF3; OCF3; CN; COOR2; d-Cealkyl; Ci-C8alkoxy; Ci-C8alkythio; Ci-C8alkyl-S02;
pyrrolidinyl; di(Ci-C4alkyl)amino; morpholinyl; phenyl substituted by phenyl or Ci-
C8alkyl; d-Cealkyl interrupted by O; Ci-dalkyl or vinyl or Ci-dalkythio or C8alkyl-S02 each
of which is substituted by CN or COOR2 or phenyl or CF3;
R16 and R17 independently are H, halogen, nitro.

The mixture is compounded with liquid crystal material; the present dye mixture is easily
dissolvable in the liquid crystal material following known techniques such as formation a pre-
solution of one or more of the dyes in a solvent, especially a solvent of high vapor pressure
such as lower alkyl ethers, hydrocarbons, or halohydrocarbons such as dichloromethane,
mixing the pre-solution with the LC material and removing the solvent under reduced pressure
and/or heating. The LC material is mostly commercially available; application of the dyes in the
liquid crystal material, types of liquid crystal material, assembly of liquid crystal cells and testing
methods are known in the art, some are described, for example, in US-4565424 (see e.g. col.
13-18). The present compounds can be prepared and, if desired, further purified according to
known methods, especially in the field of azo dye chemistry; some of these methods are also
described in US-4565424 (see e.g. col. 9-10). Novel dyes of the present invention may be
obtained and purified in accordance or analogy to present examples. The disclosure of US-
4565424, especially of the above cited passages, is hereby incorporated by reference.

The present invention thus further provides a composition, which contains the present dye
mixture (generally red and blue dye and optionally a yellow dye as described above) in
dissolved state in a liquid crystal material.

For obtaining the optimum black shade, the ratio of weight parts of the dye(s) conforming to
formula (A) to the dye(s) conforming to formula (B), i.e. (A):(B), is usually 0.1:20 to 5:1.
The dye composition may comprise 1 to 20, preferably 1 to 10, especially 1.5 to 5 parts by weight of at least one conforming to formula (B), and 0.1 to 5, especially 0.5 to 2 parts by weight of each dye conforming to the formula (A).

In case of a blue/red/yellow dye mixture, for obtaining the optimum black shade, the present dye composition usually contains about 1 to 20, e.g. 1 to 10, especially 1.5 to 5 parts by weight of the blue dye and 0.1 to 5, especially 0.5 to 2, parts by weight of the red dye on 1 part by weight of the yellow dye.

The final LC composition may contain 1 to 20 parts, preferably 1 to 10 parts, especially 1.5 to 5 parts of the dye conforming to formula (B), 0.1 to 5 parts, especially 0.5 to 2 parts of each dye conforming to formula (A), based on 50 to 2000 parts, especially 100 to 500 parts, of liquid crystal material, all parts given as parts by weight.

The final LC composition thus often contains 1 to 20 parts, for example 1 to 10 parts, especially 1.5 to 5 parts by weight of the blue dye, 0.1 to 5 parts, especially 0.5 to 2 parts by weight of the red dye, and 1 part by weight of the yellow dye, on 50 to 2000 parts, especially 100 to 500 parts by weight, of liquid crystal material.

Especially preferred is a composition containing 1 to 5% by weight of the present black dye mixture in LC material. The LC compositions usually contain the LC material as main component (i.e. 50%, especially 90% by weight or more), and may contain some further minor components (e.g. up to 49%, especially up to 9%) such as polymerization aids, additives, photoinitiators or their remainders after polymerization (all parts and percentages given by weight).

Consequently, the present invention further pertains to a liquid crystal display containing the dye composition as described, especially a liquid crystal display containing the dye composition in a polarizing film; to a process for the preparation of a polarizing film or a liquid crystal display, which process comprises dissolving a dye composition according to the invention in liquid crystal material; and to the use of the present black dichroic dye composition, or any of the novel dyes described further below, for the preparation of a polarizing film or a liquid crystal display.

Some examples for dyes useful in the present black dichroic dye compositions are as listed below:

1. Yellow Dichroic Disazo Dyes
### 2. Red Dichroic Disazo Dyes

<table>
<thead>
<tr>
<th>Structure 1</th>
<th>Structure 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td><img src="image2.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 1" /></td>
<td><img src="image4.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 1" /></td>
<td><img src="image6.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image7.png" alt="Structure 1" /></td>
<td><img src="image8.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image9.png" alt="Structure 1" /></td>
<td><img src="image10.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image11.png" alt="Structure 1" /></td>
<td><img src="image12.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image13.png" alt="Structure 1" /></td>
<td><img src="image14.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image15.png" alt="Structure 1" /></td>
<td><img src="image16.png" alt="Structure 2" /></td>
</tr>
</tbody>
</table>

---

*Note: The images are placeholders and should be replaced with actual images of the structures.*
3. Blue Dichroic Trisazo Dyes (based on aromatic components)
4. Blue Dichroic Disazo or Trisazo Dyes (with heteroaromatic components)
Some especially useful blue dyes in the present invention are novel compounds. The present invention thus further pertains to a dye which is a compound of the formula B10

\[
\text{Ar}_1 \text{N}=\text{N}\left[\text{Ar}_2 \text{N}=\text{N}\right]_q \text{Ar}_3 \text{N}=\text{N} \quad \text{(B10)}
\]

wherein

- \(q\) is 0 or 1;
- \(\text{Ar}\) is phenyl substituted by \(X_b\), or is a heterocyclic residue of one of the formulae

\[
\begin{align*}
\text{Ar}_2 & \text{ is 1,4-phenylene, 1,4-phenylene substituted by } \text{Cl-C4alkyl, or is 1,4-naphthylene;}
\end{align*}
\]
Ar₃ is 1,4-phenylene, 1,4-phenylene substituted by C₈-C₄alkyl, or is 1,4-naphthylene; Xₜ is Hal, COOR₂, CN, phenyl, Re-substituted phenyl, C₃-Ci₂cycloalkyl, Ci-Ci₂alkyl-cyclohexyl, Ci-Ci₂alkoxy-cyclohexyl; preferably Xₜ is COOR₂, phenyl, Re-substituted phenyl, C₃-Ci₂cycloalkyl, Ci-Ci₂alkyl-cyclohexyl, Ci-Ci₂alkoxy-cyclohexyl; Hal is CF₃ or fluoro; R₅ is d-Csalkyl; Rₛ is Ci-Csalkyl, Ci-Csalkoxy, C₃-Ci₂cycloalkyl, phenyl, Ci-Ci₂alkyl-phenyl, Ci-Ci₂alkyl-cyclohexyl, Ci-Ci₂alkoxy-cyclohexyl; R₁₁ is pyrrolidinyl or piperidinyl or di(Ci-C₄alkyl)amino or morpholinyl; R₁₂ and R₁₃ independently are H; Hal; CN; COOR₂; Ci-Ci₂alkyl; Ci-Ci₂alkoxy; Ci-Ci₂alkylthio; phenyl; phenyl substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C₂-Ci₂alkyl or C₃-Ci₂alkoxy or C₃-Ci₂alkylthio each of which is interrupted by O; Ci-Csalkyl or C₂-C₃alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or COOR₂ or phenyl or fluoro or CF₃; or R₁₂ and R₁₃ together are C₃-C₄alkylene; R₁₄ is H; CF₃; CN; COOR₂; Ci-Csalkyl; Ci-Csalkoxy; pyrrolidinyl, piperidinyl, di(Ci-C₄alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C₂-Ci₂alkyl or C₃-Ci₂alkoxy or C₃-Ci₂alkylthio each of which is interrupted by O; Ci-Csalkyl or C₂-C₃alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or COOR₂ or phenyl or fluoro or CF₃; R₁₅ is H; CF₃; OCF₃; CN; COOR₂; Ci-Ci₂alkyl; Ci-Ci₂alkoxy; Ci-Ci₂alkylthio; Ci-Ci₂alkyl-SO₂; pyrrolidinyl; di(Ci-C₄alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio or CN or CF₃ or OCF₃; C₂-Ci₂alkyl or C₃-Ci₂alkoxy or C₃-Ci₂alkylthio each of which is interrupted by O; Ci-Csalkyl or C₂-C₃alkenyl or Ci-Csalkoxy or Ci-Csalkylthio or Ci-C₈alkyl-SO₂ each of which is substituted by CN or COOR₂ or COR₂ or phenyl or fluoro or CF₃; R₁₆ and R₁₇ independently are H, halogen, nitro, Ci-Csalkyl, Ci-Csalkoxy, with the proviso that a compound of formula

\[
\begin{array}{c}
\text{R}_{21} \quad \text{N} \quad \text{N} \\
\text{N} \quad \text{CH}_3 \\
\text{N} \quad \text{S} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{R}_{11}
\end{array}
\]

, wherein R₂₁ is F, CF₃ or CN is excluded.

Among the dyes of formula B₁₀, preferred ones conform to formula B₁₁, B₁₂ and/or B₁₃.

\[
\begin{array}{c}
\text{Xₜ} \quad \text{N} = \text{N} - \text{Ar}_{2} \quad \text{N} = \text{N} - \text{Ar}_{3} \quad \text{N} = \text{N} \\
\text{S} \\
\text{R}_{11}
\end{array}
\]

(B₁₁)

\[
\begin{array}{c}
\text{Ar}_{q} \quad \text{N} = \text{N} - \left[ \text{Ar}_{2} \quad \text{N} = \text{N} \right]_{q} \quad \text{Ar}_{3} \quad \text{N} = \text{N} \\
\text{S} \\
\text{R}_{11}
\end{array}
\]

(B₁₂)
wherein
q is 0 or 1;

5 \( \text{Ar}_5 \) is a heterocyclic residue of the formula

\[ \text{An} \] is a heterocyclic residue of one of the formulae

\[ \text{Xb} \] is Hal, COOR\(_2\), CN, phenyl, R\(_8\)-substituted phenyl;

10 Hal is CF\(_3\) or fluoro;

R\(_2\) is d-alkyl;

R\(_8\) is c \( \pm \)Csalkyl, cyclohexyl, phenyl, c \( \pm \)Csalkyl-phenyl, c \( \pm \)Csalkyl-cyclohexyl;

R\(_{11}\) is pyrrolidinyl or d(\( \pm \)C\(_1\)-C\(_4\)alkyl)amino or morpholinyl;

R\(_{12}\) and R\(_{13}\) independently are H; Hal; CN; COOR\(_2\); c \( \pm \)Csalkyl; phenyl; phenyl substituted by phenyl or c \( \pm \)Csalkyl or cyclohexyl or c \( \pm \)Csalkoxy; C2-C\(_3\)alkyl or C\(-\)Csalkylthio each of which is interrupted by O; c \( \pm \)Csalkyl or vinyl each of which is substituted by CN or COOR\(_2\); or R\(_{12}\) and R\(_{13}\) together are C\(_3\)-C\(_4\)alkylene;

R\(_{14}\) is CF\(_3\); CN; COOR\(_2\); d-alkyl; c \( \pm \)C\(_8\)alkoxy; c \( \pm \)C\(_8\)alkylthio; pyrrolidinyl; d(\( \pm \)C\(_1\)-C\(_4\)alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or c \( \pm \)Csalkyl; C2-C\(_3\)alkyl interrupted by O; c \( \pm \)Csalkyl or vinyl or c \( \pm \)Csalkylthio each of which is substituted by CN or COOR\(_2\) or phenyl or CF\(_3\);

R\(_{15}\) is CF\(_3\); OCF\(_3\); CN; COOR\(_2\); d-alkyl; c \( \pm \)C\(_8\)alkoxy; c \( \pm \)C\(_8\)alkylthio; c \( \pm \)C\(_8\)alkyl-SO\(_2\); pyrrolidinyl; d(\( \pm \)C\(_1\)-C\(_4\)alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or c \( \pm \)C\(_8\)alkyl; C2-C\(_3\)alkyl interrupted by O; c \( \pm \)Csalkyl or vinyl or c \( \pm \)Csalkylthio or c \( \pm \)C\(_8\)alkyl-SO\(_2\) each of which is substituted by CN or COOR\(_2\) or phenyl or CF\(_3\);

R\(_{16}\) and R\(_{17}\) independently are H, halogen, nitro; and

The other symbols are as defined for formula B10;

with the proviso that a compound of formula

\[ \text{R}_{21} \] is F, CF\(_3\) or CN is excluded.
Preferably, at least one of \( \text{Ar}_2 \) and \( \text{Ar}_3 \) of formula B11 is 1,4-naphthylene.

Some examples for the novel blue dichroic dyes are the compounds listed below:

<table>
<thead>
<tr>
<th>![Chemical Structure 1]</th>
<th>![Chemical Structure 2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Chemical Structure 3]</td>
<td>![Chemical Structure 4]</td>
</tr>
<tr>
<td>![Chemical Structure 5]</td>
<td>![Chemical Structure 6]</td>
</tr>
<tr>
<td>![Chemical Structure 7]</td>
<td>![Chemical Structure 8]</td>
</tr>
<tr>
<td>![Chemical Structure 9]</td>
<td>![Chemical Structure 10]</td>
</tr>
<tr>
<td>![Chemical Structure 11]</td>
<td>![Chemical Structure 12]</td>
</tr>
<tr>
<td>![Chemical Structure 13]</td>
<td>![Chemical Structure 14]</td>
</tr>
<tr>
<td>Structure 1</td>
<td>Structure 2</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td><img src="image2.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 1" /></td>
<td><img src="image4.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 1" /></td>
<td><img src="image6.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image7.png" alt="Structure 1" /></td>
<td><img src="image8.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image9.png" alt="Structure 1" /></td>
<td><img src="image10.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image11.png" alt="Structure 1" /></td>
<td><img src="image12.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image13.png" alt="Structure 1" /></td>
<td><img src="image14.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image15.png" alt="Structure 1" /></td>
<td><img src="image16.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image17.png" alt="Structure 1" /></td>
<td><img src="image18.png" alt="Structure 2" /></td>
</tr>
<tr>
<td><img src="image19.png" alt="Structure 1" /></td>
<td><img src="image20.png" alt="Structure 2" /></td>
</tr>
</tbody>
</table>
The following examples are included for illustrative purposes only and are not to be construed to limit the scope of the claims. Unless otherwise stated, all parts and percentages are by weight. Over night denotes a time period from about 12 to 15 hours; room temperature denotes a temperature range 18-23°C; similarly ambient conditions, which also imply atmospheric pressure.

Abbreviations:
- NBS: N-bromosuccinimide
- THF: tetrahydrofuran
- TBME: tert-butyl methyl ether
- NMP: N-methylpyrrolidone
- Mn: molecular weight (number average)
- Mw: molecular weight (weight average)
- PDI: polydispersity

**Example 1**

Compound 1a: 10 parts of 2-amino-thiazole are dissolved in 100 parts of HCl (32%). 100 parts of ice and 7 parts of sodium nitrite are added in small portions. After stirring for 3 hours at -5° to 0°C 0.5 parts of sulfaminic acid are added.
Subsequently, 11 parts of m-toluidine are added, and the reaction mixture is stirred for 2 hours at 0-5°C followed by adding 40 parts of sodium chloride and further stirring for 2 hours. The precipitate is filtered off and washed with 400 parts of a 20% aq. solution of sodium chloride. The filter cake is then suspended in 500 parts of slightly alkaline water (soda), filtered, washed until neutral and dried in vacuo at 50°C. 9.5 parts of compound 1a are obtained.

![Compound 1a](image)

Compound 1b: 4.36 parts of compound 1a are dissolved in 88 parts of THF. 2.9 parts of tetrafluoroboric acid solution (50% in water) are added, followed by 2.8 parts of tert-butylnitrite within 1 minute at 15°C. After stirring for 1.5 hours at 15°C the precipitate is filtered and washed with tert-butyl methyl ether. The filter cake is then added to a solution of 2.4 parts of m-toluidine in 70 parts of methanol. After 60 minutes 6 parts of a 4N aq. solution of sodium acetate and then 30 parts of methanol are added. The dark red suspension is stirred overnight and filtered, and the residue is washed with 200 parts of methanol and dried at 60°C. 2.2 parts of a dark powder (compound 1b) are obtained.

![Compound 1b](image)

Compound 1c:
A) 1.1 parts of compound 1b are dissolved in 25 parts of N-methylpyrrolidone, and the solution is cooled to 0-5°C. 1 part of nitrosylsulfuric acid (40% in sulfuric acid) is added dropwise within 5 minutes resulting in a dark brown suspension (A) which is stirred for 1 hour.

B) 0.55 parts of 2-pyrrolidino-thiophene (prepared from 2-bromothiophene and pyrrolidine) are dissolved in 30 parts of a methanolic solution of sodium acetate (0.625 molar), and the solution is cooled to 0-5°C, followed by dropwise adding suspension (A) within 5 minutes. The resulting suspension is stirred for 2 hours at 0-5°C and is then diluted with 25 parts of water. After filtration the crude product is washed with water and dried in vacuo at 50°C. 1.15 parts of compound 1c are further purified by column chromatography (silica; toluene / ethyl acetate).

![Compound 1c](image)
Example 2

Compound 2a:

A) 15 parts of 2-amino-thiazole are dissolved in HCl (37%), 35 parts of ice are added, followed by 38 parts of a 4N solution of sodium nitrite. After 1.5 hours at -5° to 0°C 0.5 parts of sulfaminic acid are added (solution A).

B) 38 parts of sodium phenylamino-N-methanesulfonate (82%) are dissolved in 200 parts water, and the solution is cooled to 0°C (solution B). Solution A is slowly added within 0.5 hours to solution B; the pH is kept at 8.5 to 9 by adding sodium hydroxide (30%). After stirring for 3 hours at 5°C the reddish brown suspension is filtered and washed with brine (15%). The filter cake is then transferred to 500 parts of a 1N solution of sodium hydroxide, stirred for 1 hour at 70°C and kept overnight at room temperature. The precipitate is filtered off, washed with 800 parts of water and dried. 17.3 parts of compound 2a are obtained.

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

(Compound 2a)

Compound 2b: 15.3 parts of compound 2a are dissolved in 200 parts of NMP, and the solution is cooled to 0°-5°C. 24 parts of nitrosylsulfuric acid (40%) are added dropwise and stirred for 1.5 hours at 0-5°C. The resulting solution is added to a solution of 8 parts of m-toluidine in 200 parts of methanol at 0°C with stirring. Stirring is continued overnight at a temperature finally raised to 15°C. The pH is subsequently raised to 12 by adding 50 parts of sodium hydroxide (30%), while the temperature is kept at 20°C by addition of ice. Upon addition of 400 parts of water a sticky precipitate is formed which is filtered off and then dissolved in ethyl acetate. The solution is dried over sodium sulfate and evaporated to dryness. After column chromatography (silica gel; toluene / ethyl acetate), 2.7 parts of pure compound 2b are obtained.

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

(Compound 2b)

Compound 2c: 2.7 parts of compound 2b are dissolved in 50 parts of NMP, the solution is cooled to 0-5°C, and 2.6 parts of nitrosylsulfuric acid (40%) are added dropwise within 5 minutes. After stirring for 1.5 hours at 0-5°C, the solution is added slowly to a cooled (0°C) solution of 1.3 parts of 2-pyrrolidino-thiophene in 50 parts of NMP and 5.5 parts of sodium hydroxide (30%). After stirring for 30 minutes the pH is raised to 7 by adding 1.5 parts of sodium hydroxide (30%). The reaction mixture is stirred for 2 hours at 5°C, diluted with 75 parts of water and filtered. The filter cake is washed with water and then suspended in 300 parts of methanol
and stirred for 4 hours at room temperature. After filtration, rinsing with methanol and drying in vacuo, 2.5 parts of compound 2c are obtained.

![Compound 2c](image)

**Example 3**

Compound 3a: 9.4 parts of compound 1a (Example 1) are dissolved in 180 parts of NMP, and the solution is cooled to 0-5°C. 13.7 parts of nitrosylsulfuric acid (40%) are added dropwise within 20 minutes. The resulting brown suspension is stirred for 1 hour at 0-5°C and then added to a solution of 6.15 parts of 1-naphthylamine in 150 parts of methanol. After stirring for 2 hours at 0-5°C 26 parts of sodium hydroxide (30%) are added dropwise within 10 minutes, followed by 110 parts of water. The precipitate is filtered off, washed with 500 parts of water and dried at 50°C. The crude product (19.3 parts) is suspended in 500 parts of water, stirred for 2 hours, filtered, washed with 500 parts of water and dried in vacuo at 50°C for 18 hours: 12.6 parts of compound 3a.

![Compound 3a](image)

Compound 3b: 22.2 parts of compound 3a are dissolved in 220 parts of NMP, and the solution is cooled to 0°C. 19 parts nitrosylsulfuric acid are added dropwise within 10 minutes and stirred for 2 hours. 12 parts of 1-(N-2-butylamino)-naphthalene are added and stirred for 3 hours at 5°C, 220 parts of water are added and the pH is raised to 7-8 by adding 30 parts of sodium hydroxide (30%). The precipitate is filtered, washed with 1000 parts of water and dried at 50°C. 28.1 parts of crude product 3b are obtained which is recrystallized from toluene / 2-propanol.

![Compound 3b](image)

**Example 4**

Compound 4a: 9 parts of compound 2a (example 2) are dissolved in 180 parts of NMP, and the solution is cooled to 0-5°C. 14.5 parts of nitrosylsulfuric acid (40%) are added dropwise and stirred for 1 hour at 0-5°C. 6.4 parts of 1-naphthylamine (dissolved in 180 parts of methanol, cooled to 0°-5°C) are added within 5 minutes, and the reaction mixture is stirred for 3 hours at
0°-5°C. 28 parts of 2N sodium hydroxide are added dropwise within 15 minutes, followed by 350 parts of water. The precipitate is filtered, washed thoroughly with water and dried at 50°C: 11.8 parts of compound 4a.

(Compound 4a)

Compound 4b: 14.4 parts of compound 4a are dissolved in 290 parts of NMP, and the solution is cooled to 0-5°C. 12.7 parts of nitrosylsulfuric acid (40%) are added dropwise within 10 minutes and stirred for 2.5 hours at 0-5°C. 8 parts of 1-(N-2-butylamino)-naphthalene are added. After adding 100 parts of 2N sodium hydroxide and subsequently 80 parts of water, the precipitate is filtered and washed with 1000 parts of water. The filter cake is suspended in 700 parts of methanol and stirred overnight at room temperature. After filtration, the residue is washed with 1000 parts of methanol and dried at 50°C: 17.8 parts of crude product.

Recrystallization from toluene / 2-propanol yields 13 parts of pure compound 4b.

(Compound 4b)

Example 5

Compound 5a: 10 parts of 2-amino-thiazole are dissolved in 100 parts of HCl (32%). Then, 100 parts of ice and 7 parts of sodium nitrite are added in small portions and stirred for 3 hours at -5°C to 0°C. 0.5 parts of sulfaminic acid are added.

Subsequently 11 parts of o-toluidine are added, and the reaction mixture is stirred overnight at 0°C to room temperature. After adding 40 parts of sodium chloride and further stirring for 3 hours the precipitate is filtered off. The filter cake is then suspended in 250 parts of water, the pH is raised to 8.5 by adding 22 parts of 2N sodium hydroxide. The resulting mass is suspended in 250 parts of dichloromethane, stirred at room temperature for 2 hours, filtered and washed with further dichloromethane (orange solution). The residue is then suspended in 400 parts of 4N sodium hydroxide, stirred at room temperature and filtered. The filter cake is dissolved in dichloromethane, and the orange solution is dried over sodium sulfate. The combined orange dichloromethane solutions are purified over silica gel and evaporated to dryness. After drying in vacuo at 50°C, 3.9 parts of an orange powder (compound 1a) are obtained.

(Compound 5a)
Compound 5b: Proceeding with compound 5a in analogy to example 3 (compound 3a) yields compound 5b:

![Chemical Structure](image)

(Compound 5b)

Compound 5c: Proceeding like in example 3 but using compound 5b instead of compound 3a yields dyestuff 5c:

![Chemical Structure](image)

(Compound 5c)

Example 6

Compound 6a: 75 parts of 4N sodium nitrite are added with 50 minutes to a suspension of 48.6 parts of 4-trifluoromethyl-aniline in 190 parts of 1N HCl and 560 parts of ice and stirred for 2 hours at 5°C. 0.5 parts of sulfamic acid are added, and the solution is filtered. The filtered solution is then added dropwise to a cooled (5°C) solution of 60 parts of sodium phenylamino-N-methanesulfonate and 57 parts of sodium hydrogen carbonate in 450 parts of water and stirred for 2 hours at 10°C and overnight at room temperature. The reaction mass is filtered, and the residue is washed with 350 parts of brine (25%). The crude product is transferred to 800 parts of warm water (70°C), 100 parts of sodium hydroxide (30%) are added dropwise within 10 minutes and stirred for 3.5 hours at 70-75°C. The reaction mass is filtered at 60°C, washed neutrally with 5000 parts of water. Drying at 35°C in vacuo yields 72.5 parts of orange-yellow product 6a.

![Chemical Structure](image)

(Compound 6a)

Compound 6b:

A) 10.6 parts of compound 6a are dissolved in 50 parts of NMP, and 50 parts of 2N HCl are added thereto. After cooling to 0-5°C 10 parts of 4N sodium nitrite are added dropwise within 10 minutes. Diazotation is completed by stirring for 30 minutes at 0-5°C (solution A).

B) 5.8 parts of 1-naphthylamine are dissolved in 20 parts of NMP, and 20 parts of 2N HCl are added thereto. The solution is cooled to 5°C, and solution A is added over 5 minutes and stirred for 1 hour at 5-7°C. The reaction mixture is filtered, and the residue is transferred into a beaker and suspended in slightly alkaline water (500 parts). After filtration the residue is washed...
neutrally with water and dried in vacuo at 50°C. The crude product (12.2 parts) is recrystallized (toluene / hexane): 7.1 parts of pure compound 6b.

\[
\text{Compound 6b)}
\]

Compound 6c: 62 parts of compound 6b are dissolved in 1400 parts of NMP and the solution is cooled to 0°C. 47 parts of nitrosylsulfuric acid (40%) are added dropwise within 10 minutes and stirred for 1.5 hours at 0°C. 29.7 parts of 1-(N-2-butylamino)-naphthalene are added, and stirring is continued for 1.5 hours at 0-5°C. 275 parts of 4N sodium acetate are then added dropwise within 15 minutes. After stirring for 45 minutes at 5°C 300 parts of water are added within 15 minutes. After stirring for 1 hour at 10-15°C the reaction mass is filtered. The residue is washed with 2000 parts of water / methanol (1:1) and then with 2000 parts of water. The filter cake is transferred into a beaker and stirred for 1 hour with 1400 parts of methanol. After filtration the filter cake is washed with 1200 parts of methanol and dried in vacuo at 50°C: 74 parts of compound 6c.

\[
\text{Compound 6c)}
\]

Example 7

Compound 7a: 8.1 parts of 4-trifluoromethyl-aniline are added to 75 parts 2N HCl. 13 parts of 4N sodium nitrite are added within 30 minutes, and diazotation is completed by stirring at 5°C for 1 hour (solution A).

7.4 parts of 1-naphthylamine are dissolved in 75 parts of ethanol, and 75 parts of water are added. After cooling to 0-5°C solution A is added within 10 minutes. After 1 hour at 0-5°C 50 parts of 4N sodium acetate are added, and the temperature is raised to room temperature. 120 parts of water are added, the reaction mixture is filtered, and the residue is washed with 750 parts of water and dried at 50°C. 14.9 parts of product 7a are obtained.

\[
\text{Compound 7a)}
\]

Compound 7b: 4.8 parts of compound 7a are dissolved in 120 parts of THF, the solution is cooled (0-5°C), and 3 parts of tetrafluoroboric acid (50%) are added. 2.7 parts of tert-butylnitrite
are added dropwise within 1 minute and the resulting is stirred for 2 hours at 0-1.5°C. The resulting precipitate is filtered and washed with 60 parts of diethylether. The moist filter cake is transferred to a cooled solution (5°C) of 2.2 parts of 1-naphthylamine in 80 parts of methanol and the mixture is stirred for 1 hour at 5-1.5°C. The precipitate is filtered, washed with 150 parts of methanol and dried in vacuo: 2.94 parts of compound 7b.

![Compound 7b](image)

Compound 7c: 2.94 parts of compound 7b are dissolved in 60 parts of NMP. 2.0 parts of nitrosylsulfuric acid (40%) are added within 2 minutes to the cooled solution (0-5°C). Further 30 parts of NMP are added to the viscous reaction mass. After 1 hour at 0-5°C 1.25 parts of 1-(N-2-butylamino)-naphthalene are added, and after a further hour at 0-5°C 10 parts of 4N sodium acetate and subsequently 150 parts of water are added. The coupling reaction is completed by stirring for 1 hour at room temperature. The precipitate is filtered, washed with 150 parts of water and dried in vacuo at 50°C: 3.71 parts of crude product 7c which can be purified by column chromatography (silica; hexane / toluene) and recrystallization (toluene / hexane).

![Compound 7c](image)

**Example 8**

Compound 8a: 20.4 parts of 4-aminobiphenyl are suspended in 400 parts of 2N HCl, and the suspension is cooled to 5°C. 3.12 parts of sodium nitrite are added within 1 hour. After 2 hours at 5°C the solution is filtered (solution A).

17.2 parts of 1-naphthylamine are dissolved in 480 parts of water / ethanol (1:1) and the solution is cooled to 0-5°C. Solution A is then added within 20 minutes leading to a viscous reaction mixture which is diluted with 200 parts of water / ethanol. After 1 hour at 0-5°C 160 parts of 4N sodium acetate are added, and the temperature is raised to room temperature. Stirring at room temperature is continued overnight. The reaction mass is filtered, and the filter cake is suspended in 1500 parts of water. By adding of 4N sodium hydroxide the pH is raised to 8-9. The precipitate is filtered, washed with water and dried at 50°C: 33.75 parts of compound 8a.
Compound 8b: 2.1.0 parts of compound 8a are dissolved in 450 parts of sulfolane, 20.8 parts of nitrosylsulfuric acid are added within 30 minutes, and the reaction mixture is stirred for 2 hours at 18-20°C (solution A).

9.3 parts of 1-naphthylamine are dissolved in 260 parts of water / ethanol (1:1). The solution is cooled to 0-5°C, and solution A is added within 20 minutes. After 1 hour at 0-5°C 80 parts of 4N sodium acetate are added, and the temperature is raised to room temperature. The precipitate formed is filtered and washed with 500 parts of ethanol / water (1:1) and then with 1000 parts of water. The filter cake is suspended in 1000 parts of methanol, and the suspension is stirred for 1 hour at room temperature. After filtration 22.6 parts of a black powder (compound 8b) are obtained.

Compound 8c: 7.4 parts of compound 8b are dissolved in 75 parts of NMP, and the solution is cooled to 0-5°C. 4.9 parts of nitrosylsulfuric acid (40%) are added dropwise within 7 minutes while the temperature is kept at 5°C. After stirring for 15 minutes at 5°C 3 parts of 1-(N-2-butylamino)-naphthalene are added, and stirring is continued for 4 hours at 10°C. After filtration the residue is washed with 100 parts of 2-propanol / water (1:1) and dried in vacuo at 50°C: 8.9 parts of compound 8c.

Example 9
Compound 9a: 8.3 parts of 4-amino-benzoic acid ethyl ester are suspended in 75 parts of 2N HCl. After cooling to 5°C 13 parts of 4N sodium nitrite are added within 30 minutes. After further stirring for 1 hour at 5°C 0.5 parts of sulfamic acid are added (solution A). 7.4 parts of 1-naphthylamine are dissolved in 75 parts of ethanol, 75 parts of water are added, the suspension is cooled to 0-5°C, and solution A is added over 1 hour. The increasingly viscous reaction mass is diluted by adding 50 parts of ethanol, 20 parts of DMF and 100 parts of
water. After 1 hour at 0-5°C 50 parts of 4N sodium acetate are added, and the temperature is raised to room temperature. Then 300 parts of water are added, and the reaction mass is filtered. The residue is washed with 750 parts of water and dried at 50°C: 16.4 parts of compound 9a.

\[
\text{O} \quad \text{N} \quad \text{NH}_2
\]

(Compound 9a)

Compound 9b: 11.4 parts of compound 9a are dissolved in 250 parts of THF. After cooling to 0-5°C 7.2 parts of tetrafluoroboric acid (50%) and subsequently 6.4 parts of tert-butyl nitrite are added. After 2 hours at 0-15°C the residue is filtered off and washed with 150 parts of diethylether. The moist filter cake is transferred to a cooled solution (5°C) of 5.2 parts of 1-naphthylamine in 200 parts of methanol. After 1 hour at 5-15°C the reaction mixture is filtered, and the residue is washed with 300 parts of methanol and dried in vacuo at 50°C: 12.5 parts of compound 9b.

\[
\text{O} \quad \text{N} \quad \text{N} \quad \text{NH}_2
\]

(Compound 9b)

Compound 9c: 6.25 parts of compound 9b are dissolved in 130 parts of NMP, and the solution is cooled to 0-5°C. 4.2 parts of nitrosylsulfuric acid (40%) are added within 2 minutes. After stirring for 1 hour at 0-5°C 2.63 parts of 1-(N-2-butylamino)-naphthalene are added. After 1 hour at 0-5°C 30 parts of 4N sodium acetate are added, followed by 30 parts of water. After 1 hour stirring at room temperature the reaction mixture is filtered, and the residue is washed with 300 parts water and dried in vacuo at 50°C: 7.61 parts of crude product 9c. Purification of 9c is accomplished by column chromatography (silica; toluene / ethyl acetate).

\[
\text{O} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{NH}
\]

(Compound 9c)

Example 10

Compound 10a: 16.1 parts of 4-trifluoromethyl-aniiline are suspended in 125 parts of 2N HCl at 0°C, and 25 parts of 4N sodium nitrite are added at a rate of 3 parts per minute. After 2 hours stirring at 0°C 1 part of sulfamic acid is added. After filtration the resulting yellow solution is added within 45 minutes to a solution of 22.3 parts of sodium m-tolylamino-N-methanesulfonate
in 200 parts of water (pH 9). The pH is kept at 9 by adding 1 M sodium carbonate (total: 152 parts). After stirring for 4 hours at 0-5°C 100 parts of NaOH (30%) are added, and the reaction mixture is stirred at 45-50°C for 6 hours. The precipitate is filtered off, washed with 1000 parts of water and dried in vacuo at 60°C: 26.2 parts of compound 10a.

\[
\begin{align*}
\text{F}_3\text{C}- & \text{N} \quad \text{N} \quad \text{NH}_2 \\
\text{CH}_3 & \\
\end{align*}
\]

(Compound 10a)

Compound 10b: 40 parts of compound 10a are suspended in 350 parts of acetic acid and 31.7 parts of nitrosylsulfuric acid are added dropwise at 10°C within 15 minutes. Stirring is continued for 1 hour at 5°C (solution A).

14.7 parts of phenyl-pyrrolidine are dissolved in 180 parts of acetic acid. Then 26.5 parts of sodium acetate are added, and after cooling to 0°C solution A is added within 10 minutes. The temperature is kept at 0-5°C by adding ice. After 1 hour at 5-10°C 100 parts of 1N NaOH are added dropwise. The precipitate is filtered off after 10 minutes, washed first with 800 parts of 2-propanol / water (1:1) and then with 600 parts of ice cold 2-propanol and dried in vacuo at 50°C: 42 parts of crude product 10b which are recrystallized from toluene / 2-propanol.

\[
\begin{align*}
\text{F}_3\text{C}- & \text{N} \quad \text{N} \quad \text{N} \quad \text{CH}_3 \\
\end{align*}
\]

(Compound 10b)

Example 11

Compound 11a: 10.7 parts of m-toluidine are dissolved in 125 parts of 2N HCl. The solution is cooled to 0°C and 25 parts of 4N sodium nitrite are added within 10 minutes. Diazotation is completed by stirring for 1 hour (solution A).

10.7 parts of m-toluidine are dissolved in 250 parts of methanol. 26 parts of sodium acetate trihydrate are added, followed by solution A dropwise within 5 minutes. After stirring at 5-10°C for 2 hours methanol is evaporated in vacuo, the residue is filtered off and washed with water.

The filter cake is dissolved in 500 parts of toluene, the toluene phase is separated from the aqueous phase and dried over sodium sulfate. The dried toluene solution is filtered over silica and evaporated. The resulting dark red oil is dissolved in 30 parts of toluene and after adding 200 parts of n-hexane crystals start to form. After filtration, washing with n-hexane and drying in vacuo at 50°C 12 parts of compound 11a are obtained.

\[
\begin{align*}
\text{CH}_3 & \\
\text{N} & \\
\text{NH}_2 & \\
\text{CH}_3 & \\
\end{align*}
\]

(Compound 11a)

Compound 11b: 4 parts of compound 11a are dissolved in 60 parts of NMP and 5.6 parts of nitrosylsulfuric acid (40%) are added at 0-5°C. After stirring for 1 hour at this temperature 2.7
parts of phenyl-pyrrolidine are added and stirring is continued at 0-5°C overnight. Then the pH is raised to 7-8 by adding 50 parts of 2N NaOH, the residue is filtered off, washed with 500 parts of water and dried at 50°C: 4.5 parts of compound 11b. The crude product is recrystallized from toluene / hexane.

![Structure](https://example.com/structure.png)

(Compound 11b)

**Example 12**

Compound 12a: 4 parts of compound 11a are dissolved in 60 parts of NMP, 5.6 parts of nitrosylsulfuric acid (40%) are added at 0-5°C, and diazotation is completed by stirring at 0-5°C for 1 hour (solution A).

9.2 parts of sodium acetate trihydrate are dissolved in 180 parts of methanol / water (3:1) and 2.9 parts of phenyl-morpholine are added. After cooling to 0-5°C solution A is added slowly. After stirring at 0°C to room temperature overnight the pH is raised to 7-8 by addition of 50 parts of 2N NaOH. The precipitate is filtered off, washed with 500 parts of water and dried at 50°C: 6 parts of crude compound 12a. The crude product is recrystallized from toluene / n-hexane.

![Structure](https://example.com/structure.png)

(Compound 12a)

**Example 13**

Compound 13a: 11.2 parts of 4-fluoroaniline are dissolved in 125 parts of 2N HCl, and after cooling to 0°C 25 parts of 4N sodium nitrite are added at a rate of 3 parts per minute. After stirring for 1 hour at 0°C 1 part of sulfamic acid is added (solution A).

22.3 parts of sodium m-tolylamino-N-methanesulfonate are dissolved in 200 parts of water at 5°C, and the pH is raised to 9 with 1M sodium carbonate. Solution A is then added dropwise within 45 minutes while the pH is kept at 9 by adding 137 parts of 1 M sodium carbonate. Coupling is completed by stirring for 4 hours at 0-5°C and then at room temperature overnight. 100 parts of NaOH (30%) are added, and after 45 minutes the temperature is raised to 45°C for 6 hours. The precipitate is filtered off, washed with 800 parts of water and dried in vacuo at 60°C: 21.3 parts of compound 13a.

![Structure](https://example.com/structure.png)

(Compound 13a)
Compound 13b: 43 parts of compound 13a are dissolved in 500 parts of NMP. After cooling to 0°C 59.3 parts of nitrosylsulfuric acid are added dropwise within 15 minutes. Diazotation is completed by stirring for 2 hours at 0°C. 30.5 parts of phenyl-morpholine are dissolved in 100 parts of NMP, 95 parts of 2N HCl are added, followed by solution A within 20 minutes. After 1 hour at 0°C 40 parts of sodium acetate trihydrate are added. Three further portions of 40 parts of sodium acetate trihydrate are added after one further hour each. After stirring at 0°C to room temperature overnight 500 parts of water are added within 30 minutes, and the precipitate is filtered off and dried. The filter cake is suspended in 250 parts of 2-propanol and the suspension is stirred at 75°C for 30 minutes. After cooling to 0°C the precipitate is filtered, washed with cold (0°C) 2-propanol and dried in vacuo at 50°C: 24 parts of compound 13b. The crude product is recrystallized from toluene / 2-propanol.

![Compound 13b](image)

**Example 14:** Application in LC material

1.5 parts of compound 1c from example 1 are mixed well with 100 parts of Licrystal™ (Merck, Germany) BL006 and about 500 parts of dichloromethane. After removing the solvent by evaporation at room temperature the dye-LC mixture is heated above the clearing point of the LC material (140°C), and a droplet of the material is put at the opening of a small LC-cell (about 1 x 1 cm², the two glass substrates coated with anti-parallel rubbed polyimide, cell cap about 5 μm) and placed on a hot plate at 140°C. The cell is filled by capillary forces. After filling the cell is gently cooled down to room temperature. The dichroic ratio is measured on an Agilent spectrophotometer with the help of a polarizer: The cell is placed with the rubbing direction of the polyimide parallel and perpendicular to the polarization direction of the polarizer. The dichroic ratio is calculated by the ratio of parallel (A//) and perpendicular (A⊥) absorbance at the maximum absorption in the perpendicular state: $\text{DR} = \frac{A_{\perp}}{A_{\parallel}}$.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Absorption Maximum</th>
<th>Maximum Absorbance</th>
<th>Dichroic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="image" /></td>
<td>630 nm, 630 nm</td>
<td>$A_{\perp} = 1.94$, $A_{\parallel} = 2.12$</td>
<td>DR = 12.4, DR = 13.1</td>
</tr>
</tbody>
</table>

**Examples 15 and 16:** Application in LC material

Proceeding as indicated in example 14 with the compound below.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Absorption Maximum</th>
<th>Maximum Absorbance</th>
<th>Dichroic Ratio</th>
</tr>
</thead>
</table>
Examples 17 to 26: Application in LC material
Proceeding as indicated in example 14, but applying 3 parts instead of 1.5 parts of the corresponding dye as shown in the table below the following absorption maxima, maximum absorbances and dichroic ratios have been found:

<table>
<thead>
<tr>
<th>Structure</th>
<th>Absorption Maximum</th>
<th>Maximum Absorbance</th>
<th>Dichroic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>630 nm</td>
<td>2.69</td>
<td>12.4</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>639 nm</td>
<td>2.55</td>
<td>10.8</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>630 nm</td>
<td>2.81</td>
<td>11.0</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>650 nm</td>
<td>1.79</td>
<td>9.9</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>625 nm</td>
<td>3.09</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Examples 27 and 28: Application in LC material

Proceeding as indicated in example 14, but applying 2 parts instead of 1.5 parts of the corresponding dye as shown in the table below the following absorption maxima, maximum absorbances and dichroic ratios have been found:

<table>
<thead>
<tr>
<th>Structure</th>
<th>Absorption Maximum</th>
<th>Maximum Absorbance</th>
<th>Dichroic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>610 nm</td>
<td>3.09</td>
<td>12.4</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>612 nm</td>
<td>2.52</td>
<td>12.9</td>
</tr>
</tbody>
</table>
Examples 29 to 88: Application in LC material
Proceeding in analogy to examples 15 to 22 by applying 3 parts of the corresponding dichroic dye in 100 parts of Licrystal BL006, the following absorption maxima (nm), maximum absorbances A and dichroic ratios DR (in brackets) have been observed (table below):

<table>
<thead>
<tr>
<th>Example</th>
<th>Absorption Maxima (nm)</th>
<th>Maximum Absorbance A</th>
<th>Dichroic Ratio DR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 29</td>
<td>461 nm</td>
<td>2.20</td>
<td>10.5</td>
</tr>
<tr>
<td>Ex. 30</td>
<td>474 nm</td>
<td>1.82</td>
<td>11.4</td>
</tr>
<tr>
<td>Ex. 31</td>
<td>457 nm</td>
<td>2.55</td>
<td>13.0</td>
</tr>
<tr>
<td>Ex. 32</td>
<td>468 nm</td>
<td>2.02</td>
<td>10.1</td>
</tr>
<tr>
<td>Ex. 33</td>
<td>460 nm</td>
<td>2.23</td>
<td>7.4</td>
</tr>
<tr>
<td>Ex. 34</td>
<td>475 nm</td>
<td>1.91</td>
<td>10.7</td>
</tr>
<tr>
<td>Ex. 35</td>
<td>504 nm</td>
<td>2.65</td>
<td>10.2</td>
</tr>
<tr>
<td>Ex. 36</td>
<td>526 nm</td>
<td>2.17</td>
<td>13.3</td>
</tr>
<tr>
<td>Ex. 37</td>
<td>504 nm</td>
<td>2.99</td>
<td>10.7</td>
</tr>
<tr>
<td>Ex. 38</td>
<td>525 nm</td>
<td>2.62</td>
<td>12.5</td>
</tr>
<tr>
<td>Ex. 39</td>
<td>497 nm</td>
<td>2.77</td>
<td>8.5</td>
</tr>
<tr>
<td>Ex. 40</td>
<td>523 nm</td>
<td>2.65</td>
<td>13.2</td>
</tr>
<tr>
<td>Ex. 41</td>
<td>515 nm</td>
<td>0.85</td>
<td>9.4</td>
</tr>
<tr>
<td>Ex. 42</td>
<td>527 nm</td>
<td>2.15</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>Ex. 43 (477 nm / ( A = 2.28 ) / DR = 11.2)</td>
<td>Ex. 44 (495 nm / ( A = 1.99 ) / DR = 11.1)</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---------------------------------------------</td>
<td>---------------------------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ex. 45 (489 nm / ( A = 3.07 ) / DR = 12.8)</td>
<td>Ex. 46 (510 nm / ( A = 2.03 ) / DR = 13.2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ex. 47 (500 nm / ( A = 2.96 ) / DR = 10.9)</td>
<td>Ex. 48 (526 nm / ( A = 2.42 ) / DR = 11.0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ex. 49 (495 nm / ( A = 2.43 ) / DR = 9.0)</td>
<td>Ex. 50 (530 nm / ( A = 1.32 ) / DR = 8.1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ex. 51 (510 nm / ( A = 2.22 ) / DR = 9.3)</td>
<td>Ex. 52 (510 nm / ( A = 2.14 ) / DR = 10.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ex. 53 (469 nm / ( A = 2.30 ) / DR = 11.5)</td>
<td>Ex. 54 (520 nm / ( A = 2.52 ) / DR = 10.7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ex. 55 (475 nm / ( A = 2.07 ) / DR = 8.9)</td>
<td>Ex. 56 (525 nm / ( A = 2.65 ) / DR = 10.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ex. 57 (525 nm / ( A = 2.65 ) / DR = 10.3)</td>
<td>Ex. 58 (495 nm / ( A = 1.99 ) / DR = 11.1)</td>
<td></td>
</tr>
<tr>
<td>Ex. 59 (461 nm / A = 2.20 / DR = 10.5)</td>
<td>Ex. 60 (474 nm / A = 1.82 / DR = 11.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>--------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex. 61 (457 nm / A = 2.55 / DR = 13.0)</td>
<td>Ex. 62 (468 nm / A = 2.02 / DR = 10.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex. 63 (460 nm / A = 2.23 / DR = 7.4)</td>
<td>Ex. 64 (475 nm / A = 1.91 / DR = 10.7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex. 65 (504 nm / A = 2.65 / DR = 10.2)</td>
<td>Ex. 66 (526 nm / A = 2.17 / DR = 13.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex. 67 (504 nm / A = 2.99 / DR = 10.7)</td>
<td>Ex. 68 (525 nm / A = 2.62 / DR = 12.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex. 69 (497 nm / A = 2.77 / DR = 8.5)</td>
<td>Ex. 70 (523 nm / A = 2.65 / DR = 13.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex. 71 (515 nm / A = 0.85 / DR = 9.4)</td>
<td>Ex. 72 (527 nm / A = 2.15 / DR = 7.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex. 73 (477 nm / A = 2.28 / DR = 11.2)</td>
<td>Ex. 74 (495 nm / A = 1.99 / DR = 11.1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Examples 89 and 90: Application in LC material
Proceeding as indicated in example 14, but applying 2 parts instead of 1.5 parts of the corresponding dye as shown in the Table below the following absorption maxima, maximum absorbances and dichroic ratios have been found:
<table>
<thead>
<tr>
<th>Structure</th>
<th>Absorption Maximum</th>
<th>Maximum Absorbance</th>
<th>Dichroic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>517 nm</td>
<td>2.42</td>
<td>11.9</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>605 nm</td>
<td>2.96</td>
<td>11.7</td>
</tr>
</tbody>
</table>

**Example 9.1: Dichroic Black (Mixture)**

A mixture of 5.0 parts of compound 1c (example 1), 2.0 parts of compound 10b (example 10) and 2.0 parts of compound 13b (example 13) are mixed together with 267 parts of Licrystal™ BL006 and about 1200 parts of dichloromethane and applied as indicated in example 14. A neutral black shade is obtained.

The mixture is very well suited for polarizer applications, for contrast enhancement films (LC displays), in polymer network liquid crystals (PNLC), in polymer dispersed liquid crystals (PDLC), e-Book applications, reflective displays and many other liquid crystal applications.

**Example 9.2: Dichroic Black (Mixture)**

A mixture of 6.0 parts of compound 6c (example 6), 2.0 parts of compound 10b (example 10) and 2.0 parts of compound 13b (example 13) are mixed together with 267 parts of Licrystal™ BL006 and about 1200 parts of dichloromethane and applied as indicated in example 14. The dichroic ratio of the resulting neutral black is 9.1. An absorption spectrum recorded in the range of 400 - 800 nm using a 5 micron LC cell documents the black shade obtained and the dichroic properties of the mixture; the maximum absorbance A is about 1.8 (see fig. 1).

The mixture is very well suited for polarizer applications, for contrast enhancement films (LC displays), in polymer network liquid crystals (PNLC), in polymer dispersed liquid crystals (PDLC), e-Book applications, reflective displays and many other liquid crystal applications.

**Example 9.3: Dichroic Black (Mixture)**

4.8 parts of compound 1c (example 1) and 3.2 parts of compound 11b (example 1) are mixed together with 267 parts of Licrystal™ BL006 and about 1200 parts of dichloromethane and applied as indicated in example 14. The maximum absorbance A is 2.3, and the dichroic ratio DR is 12.1.

The mixture is very well suited for polarizer applications, for contrast enhancement films (LC displays), in polymer network liquid crystals (PNLC), in polymer dispersed liquid crystals (PDLC), e-Book applications, reflective displays and many other liquid crystal applications.
Comparative Example:
10 parts of a commercially available black mixture (Black S-428, manufactured by Mitsui Chemicals; a mixture of a yellow and a red azo dye and a blue anthraquinone dye) is mixed with 267 parts of Licrystal™ BL006 and about 1200 parts of dichloromethane and applied as in example 14. The maximum absorbance A is 1.0.

Comparing example 92 and the comparative example results in a distinctly higher color strength of the inventive black composition, i.e. the concentration of the dye mixture can be significantly reduced to achieve a suitable saturation.

Example 94: Polarizing Film
200 parts of Paliocolor® 242 (polymerisable LC material containing two residues of the formula -O-Chb-Chb-Cl-b-acrylate; BASF Germany) is mixed with 6 parts of compound 6c (example 6), 2 parts of compound 10b (example 10) and 2 parts of compound 13b (example 13) and 5 parts of Irgacure® 907 (BASF Germany). This mixture is dissolved in 1000 parts of dichloromethane.

The solution is spin-coated on a polyimide (Daxin DA 7013, Taiwan) coated glass substrate, which had been subjected to parallel rubbing. Subsequently, the glass substrate is heated on a hot plate to 130°C for 2 minutes, and slowly cooled down to room temperature. The coated glass substrate is then exposed to a medium pressure UV lamp for about 15 seconds (i.e. approximately 150mJ/cm²).

The result obtained is checked by placing the coated glass substrate on a conventional polariser. The percentage of incident light passing in the region of 400-700 nm is determined by means of a UV-VIS spectrophotometer (Agilent® 8453). By turning the polarisation direction parallel or perpendicular to the rubbing direction of the polyimide, a clear anisotropic effect is observed: Part of the light in the visual region is transmitted in the parallel configuration (>30 %), and almost no light (less than 3 %) is transmitted in the perpendicular configuration.

The film is well suited for use as an in-cell polariser.

Brief description of the figure:
Fig. 1 shows the absorption properties in visual range of the black mixture of example 92 in a LC cell (black line: parallel absorbance (A//); bold-type black line: perpendicular (A⊥) absorbance).
Claims

1. A composition comprising 2 or more dyes, wherein at least one dye conforms to the formula A

\[
\begin{array}{c}
\text{X} \quad (R_2)_m \text{N} \quad (R_3)_n \quad (R_4)_o \text{N} \quad (R_5)_p \text{N} \quad R_1 \quad R_3
\end{array}
\]

(A),

and at least one dye conforms to the formula B

\[
\text{Ar}_i\text{N}=\text{N}-[\text{Ar}_2\text{N}=\text{N}]_q\text{Ar}_3\text{N}=\text{N}\text{Ar}_4
\]

(B), wherein each of \(n\), \(m\), \(p\) is a number from 0 to 2;
\(q\) is 0 or 1;
\(A_n\) is a residue of one of the formulae

\[
\begin{array}{c}
\text{Ri} \quad (R_2)_m \text{N} \quad (R_3)_n \quad (R_4)_o \text{N} \quad (R_5)_p \text{N} \quad R_1 \quad R_3
\end{array}
\]

Ar2 is 1,4-phenylene, 1,4-phenylene substituted by one or two residues \(R_s\) or is 1,4-naphthylene;
Ar3 is 1,4-phenylene, 1,4-phenylene substituted by one or two residues \(R_s\) or is 1,4-naphthylene;
\(A_{r_4}\) is naphthyl substituted by one or two residues d-Csalkylamino or d\((\text{Ci-C8alkyl})\text{amino}\) or d\((\text{Ci-C8alkyl})\text{amino}\) whose alkyl groups are linked together to form one common bridging group Ci-Csalkylene or C2-Csalkylene interrupted by O, S and/or NR'3, or by two residues Ci-Calkylamino whose alkyl groups are linked together to form one common bridging group Ci-Csalkylene or C2-Csalkylene interrupted by O, S and/or NR'3; or \(A_{r_4}\) is thiophenyl substituted by \(R_{11}\) and optionally further substituted by d-Csalkyl or phenyl or halogen or CN, \(A_{r_4}\) especially conforming to the formula

\[
\begin{array}{c}
\text{Ri} \quad (R_2)_m \text{N} \quad (R_3)_n \quad (R_4)_o \text{N} \quad (R_5)_p \text{N} \quad R_1 \quad R_3
\end{array}
\]

\(R_i\) is Ci-Ci2alkyl, C3-C2cycloalkyl, or C3-C3cycloalkyl interrupted by O, S or NR'3, each of which alkyl or cycloalkyl is unsubstituted or substituted;
\(R_3\) is H or is as defined for \(R_i\);
or \(R_1\) and \(R_3\) together are C2-Ci2alkylene or d-Csalkylene interrupted by O, S and/or NR'3, each of which is unsubstituted or substituted, \(R_i\) and \(R_3\) thus forming, together with the nitrogen atom they are attached to, an aliphatic N-heterocyclic residue of 2 to 12 carbon atoms;
\(R'_{3}\) is H or d-Cealkyl;
each of the residues R4, R5 and R6, if present, are independently selected from unsubstituted or substituted Ci-C4 alkyl, Ci-C4 alkoxy, halogen, CN;

X is selected from H, Hal, COOR2;

Xb is Hal, COOR2, CN, phenyl. Re-substituted phenyl, C3-Ci2cycloalkyl, Ci-Ci2alkyl-cyclohexyl, a yellow dye, and the dye of formula B comprises a blue dye, which composition is a black dichroic dye composition.

Let

\[ \text{R1 is NR'R'', with R' and R'' independently selected from H or Ci-C4 alkyl or C3-Ci2cycloalkyl or phenyl or substituted phenyl; or R' and R'' together forming one common bridging group Ci-Csalkylene or C2-Csalkylene interrupted by O, S and/or NR3; R11 especially being pyrrolidinyl or morpholinyl; R12 and R13 independently are H; Hal; nitro, formyl; SCN; CN; COOR2; COR2; Cl-Ci2alkyl; Cl-Ci2alkoxy; Cl-Ci2alkythio; Cl-Ci2alkylthio; Cl-Ci2alkyl-SO2; phenyl; phenoxy; phenyl-SO2; phenyl or phenoxy or phenyl-SC2 each of which is substituted by phenyl or Ci-Csalkyl or cyclohexyl or Ci-Csalkoxy or Cl-Csalkythio; C2-Ci2alkyl or C3-Ci2alkoxy or C3-Ci2alkylthio each of which is interrupted by O; Cl-Csalkyl or C2-C3alkenyl or Cl-Csalkoxy or Cl-Csalkythio each of which is substituted by CN or COOR2 or phenyl or fluoro or CF3; or R12 and R13 together are C3-C4alkylene; R14 is H; Hal; CN; SCN; COOR2; COR2; C3-Ci2alkyl; C3-Ci2cycloalkyl; Cl-Ci2alkoxy; Cl-Ci2alkylthio; Cl-Ci2alkylamino; di(Ci-Ci2alkyl)amino; pyrrolidinyl; piperidinyl; morpholinyl; phenyl; phenyl-SO2; phenyl substituted by phenyl or Cl-Csalkyl or cyclohexyl or Ci-Csalkoxy or Cl-Csalkythio; C2-Ci2alkyl or C3-Ci2alkoxy or C3-Ci2alkylthio each of which is interrupted by O; Cl-Csalkyl or C2-C3alkenyl or Cl-Csalkoxy or Cl-Csalkythio each of which is substituted by CN or COOR2 or phenyl or fluoro or CF3; or R12 and R13 together are C3-C4alkylene; R15 is H; Hal; OCF3; CN; COOR2; COR2; Cl-Ci2alkyl; Cl-Ci2alkoxy; Cl-Ci2alkylthio; Cl-Ci2alkylamino; di(Ci-Ci2alkyl)amino; Cl-Ci2alkyl-CONH; Cl-Ci2alkyl-SO2; pyrrolidinyl; di(Ci-Ci2alkyl)amino; morpholinyl; phenyl; phenyl-SO2; phenyl or phenyl-SO2 substituted by phenyl or Cl-Csalkyl or cyclohexyl or Cl-Csalkoxy or Cl-Csalkythio or CN or CF3 or OCF3; C2-Ci2alkyl or C3-Ci2alkylthio each of which is interrupted by O; Cl-Csalkyl or C2-C3alkenyl or Cl-Csalkoxy or Cl-Csalkythio or Cl-C3alkyl-SO2 each of which is substituted by CN or COOR2 or COR2 or phenyl or Re-substituted phenyl or fluoro or CF3; R16 and R17 independently are H, halogen, nitro, Cl-Csalkyl, Cl-Csalkoxy; where any substituent of alkyl moieties mentioned is preferably selected from halogen, CF3, CN, OH, Ci-Ci4alkyl, Ci-C4alkoxy, phenyl; Cl-Csdialkylamino, or a N-bonded aliphatic or aromatic heterocyclic ring containing 2 to 5 carbon ring atoms and optionally one oxygen ring atom besides the bonding nitrogen atom.

2. The composition according to claim 1, wherein the at least one dye of formula A comprises a red dye and optionally a yellow dye, and the dye of formula B comprises a blue dye, which composition is a black dichroic dye composition.
3. The composition according to any one of claims 1 to 2, wherein compounds of the formula A conform to the formula A1

\[
X - \overset{(R_4)_m}{\text{N}} - \overset{(R_5)_n}{\text{N}} - \overset{R_1}{\text{N}} - \overset{R_3}{\text{N}}
\]

(A1)

wherein \( m \) is 0 or 1, \( R_4 \) and \( R_5 \), if present, are selected from Cl-C\(_4\)alkyl, Hal is F or CF\(_3\), and all other symbols are as defined in claim 1.

4. The composition according to any one of claims 1 to 3, wherein the yellow dye conforms to formula A or A1 with the moiety \(-N(R_i)R_3\) being morpholinyl and any of \( R_4, R_5, R_6 \), if present, being methyl; and

the red dye conforms to formula A or A1 with the moiety \(-N(R_i)R_3\) being pyrrolidinyl or piperidinyl or d(Cl-C\(_4\)alkyl)amino, and any of \( R_4, R_5, R_6 \), if present, being methyl; and

the dye of formula B is a blue dye conforming to one of the formulae B1, B2, B3, B4

wherein, in any of the formulae B1, B2, B3 and B4,
q is 0 or 1;  
Ar is 1,4-phenylene; 1,4-phenylene substituted by methyl; or is 1,4-naphthylene;  
An is a residue of one of the formulae

\[
\begin{align*}
\text{formula} \quad & \quad \text{formula} \\
\text{formula} \quad & \quad \text{formula}
\end{align*}
\]

5 Ar3 is 1,4-phenylene, 1,4-phenylene substituted by one or two methyl, or is 1,4-naphthylene;  
Xb is Hal, COOR2, CN, phenyl, substituted phenyl, cyclohexyl, c ± Ci2alkyl-cyclohexyl;  
Hal is CF3 or fluoro;  
R2 is d-Cealkyl;  
X is c ± Csalkyl, cyclohexyl, c ± Csalkyl-cyclohexyl;  
R11 is pyrrolidinyl or piperidinyl or di(c1-C4alkyl)amino or morpholinyl;  
R12 and R13 independently are H; Hal; CN; COOR2; d-Csalkyl; phenyl; phenyl substituted byphenyl or c ± Csalkyl or cyclohexyl or c ± Csalkoxy; d-Csalkyl or c ± Csalkylthio each of which isinterrupted by O; c ± Csalkyl or vinyl each of which is substituted by CN or COOR2; or R12 andR13 together are C3-C4alkylene;  
R14 is CF3; CN; COOR2; d-Cealkyl; c ± Csalkoxy; c ± C8alkylthio; pyrrolidinyl; di(c1-C4alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or c ± Csalkyl; d-Csalkylinterrupted by O; c ± Csalkyl or vinyl or c ± Csalkylthio each of which is substituted by CN orCOOR2 or phenyl or CF3;  
R15 is CF3; OCF3; CN; COOR2; d-Cealkyl; c ± Csalkoxy; c ± C8alkylthio; c ± C8alkyl-S02;  
R16 and R17 independently are H, halogen, nitro;  
R18 is H or d-Csalkylamino;  
R19 is H or d-Csalkylamino;  
R20 is H or c ± Csalkyl;  
or the alkyl groups of R18 and R19 form a common bridging group c ± C3alkylene; and all other symbols defined in analogy to claim 1.

5. The composition according to any one of claims 1 to 4, containing a compound A2

\[
\begin{align*}
\text{Hal} \quad & \quad \text{(CH3)}_n \\
\text{A2}
\end{align*}
\]

and a compound A3
and at least one of the compounds B6, B6', B7, B8, B10

wherein Hal is fluoro or CF3;
n is a number from 0 to 2;
Rig is branched C3-Calkyl and R20 is H, or R19 and R20 are C1-C4alkyl; and
R2 is linear or branched d-C3alkyl;
q is 0 or 1;
An is phenyl substituted by Xb, or is a heterocyclic residue of one of the formulae
Ar2 is 1,4-phenylene, 1,4-phenylene substituted by Ci-C4alkyl, or is 1,4-naphthylene;
Ar3 is 1,4-phenylene, 1,4-phenylene substituted by Ci-C4alkyl, or is 1,4-naphthylene;
Xb is Hal, COOR2, CN, phenyl, Re-substituted phenyl, C3-Ci2cycloalkyl, Ci-Ci2alkyl-cyclohexyl,

5  Ci-Ci2alkoxy-cyclohexyl;
Hal is CF3 or fluoro;
R5 is Ci-Csalkyl, Ci-Csalkoxy, C3-Ci2cycloalkyl, phenyl, Ci-Ci2alkyl-phenyl, Ci-Ci2alkyl-
cyclohexyl, Ci-Ci2alkoxy-cyclohexyl;
R11 is pyrrolidinyl or piperidinyl or di(Ci-C4alkyl)amino or morpholinyl;

10 R12 and R13 independently are H; Hal; CN; COOR2; Ci-Ci2alkyl; Ci-Ci2alkoxy; Ci-Ci2alkylthio;
phenyl; phenyl substituted by phenyl or Ci-CSalkyl or cyclohexyl or Ci-CSalkoxy or Ci-
Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy C3-Ci2alkylthio each of which is interrupted by O; Ci-
Csalkyl or C2-C3alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or
COOR2 or phenyl or fluoro or CF3; or R12 and R13 together are C3-C4alkylene;

15 R4 is H; CF3; CN; COOR2; Ci-Csalkyl; Ci-Csalkoxy; Ci-Csalkylthio; pyrrolidinyl; piperidinyl;
di(Ci-C4alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or Ci-Csalkyl or
cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy C3-Ci2alkylthio each of
which is interrupted by O; Ci-Csalkyl or C2-C3alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of
which is substituted by CN or COOR2 or phenyl or fluoro or CF3;

20 R5 is H; CF3; OCF3; CN; COOR2; Ci-Ci2alkyl; Ci-Ci2alkoxy; Ci-Ci2alkylthio; Ci-Ci2alkyl-S02;
pyrrolidinyl; di(Ci-C4alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or Ci-Csalkyl or
cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C2-Ci2alkyl or C3-Ci2alkoxy C3-Ci2alkylthio each of
which is interrupted by O; Ci-Csalkyl or C2-C3alkenyl or Ci-Csalkoxy or Ci-Csalkylthio or Ci-
Csalkyl-SC^ each of which is substituted by CN or COOR2 or phenyl or fluoro or CF3;

25 R16 and R17 independently are H, halogen, nitro, Ci-Csalkyl, C1-C12alkoxy.

6. The composition according to any one of claims 1 to 3, wherein one dye conforms to formula

![](image)

(A4)

30 wherein X is H, m is 1, n is 0, 1 or 2,
R4 and R5 are methyl,
and the moiety -N(Ri)R3 is pyrrolidinyl;
and at least one compound of formulae B1, B2, B3 or B4 as defined in claim 4.
7. The composition according to any one of claims 1 to 6, containing the dyes dissolved in liquid crystal material.

8. The composition according to any one of claims 1 to 7, wherein the ratio of weight parts of the dye(s) conforming to formula (A) to the dye(s) conforming to formula (B) is of from 0.1:20 to 5:1.

9. The composition according to claim 7 or 8, containing 1 to 20 parts, preferably 1 to 10 parts, especially 1.5 to 5 parts of the dye conforming to formula (B), 0.1 to 5 parts, especially 0.5 to 2 parts of each dye conforming to formula (A), based on 50 to 2000 parts, especially 100 to 500 parts, of liquid crystal material, all parts given as parts by weight.

10. A liquid crystal display containing the dye composition of any one of claims 1 to 9.

11. The liquid crystal display according to claim 10 containing the dye composition in a polarizing film.

12. A compound of the formula B10

\[
\begin{align*}
\text{Ar}_1 & \quad \text{N} = \text{N} \quad \bigg[ \text{Ar}_2 \quad \text{N} = \text{N} \bigg] \quad \text{Ar}_3 \quad \text{N} = \text{N} \\
\quad & \quad \text{S} \quad \text{R}_{11}
\end{align*}
\]

(B10)

wherein
q is 0 or 1;
An is phenyl substituted by Xb, or is a heterocyclic residue of one of the formulae

\[
\begin{align*}
\text{Ar}_2 & \quad \text{is} \quad 1,4\text{-phenylene,} \quad 1,4\text{-phenylene substituted by Ci-C4alkyl, or is 1,4-naphthylene;} \\
\text{Ar}_3 & \quad \text{is} \quad 1,4\text{-phenylene,} \quad 1,4\text{-phenylene substituted by Ci-C4alkyl, or is 1,4-naphthylene;} \\
\text{Xb} & \quad \text{is} \quad \text{Hal, COOR}_2, \quad \text{CN, phenyl, Re-substituted phenyl, C}_3\text{-Si}2\text{cycloalkyl, Ci-Ci2alkyl-cyclohexyl, Ci-Ci2alkoxy-cyclohexyl;} \\
\text{Hal} & \quad \text{is} \quad \text{CF}_3 \quad \text{or fluoro;} \\
\text{R}_2 & \quad \text{is} \quad \text{d-Cealkyl;} \\
\text{Rs} & \quad \text{is} \quad \text{Ci-Ci2alkyl, Ci-Ci2alkoxy, C}_3\text{-Ci2cycloalkyl, phenyl, Ci-Ci2alkyl-phenyl, Ci-Ci2alkyl-cyclohexyl, Ci-Ci2alkoxy-cyclohexyl;} \\
\text{R11} & \quad \text{is} \quad \text{pyrrolidinyl or piperidinyl or di(Ci-C4alkyl)amino or morpholinyl;} \\
\text{R12} \quad \text{and} \quad \text{R13} & \quad \text{independently are} \quad \text{H; Hal; CN; COOR}_2; \quad \text{Ci-Ci2alkyl;} \quad \text{Ci-Ci2alkoxy; Ci-Ci2alkylthio; phenyl; phenyl substituted by phenyl or C-i-Csalkyl or cyclohexyl or Ci-Csalkoxy or Ci-}
\end{align*}
\]
Csalkylthio; C₂-C₅alkyl or C₃-C₁₂alkoxy or C₃-C₁₂alkylthio each of which is interrupted by O; Ci-
Csalkyl or C₂-C₁₂alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of which is substituted by CN or
COOR₂ or phenyl or fluoro or CF₃; or R₁₂ and R₁₃ together are C₃-C₄alkylene;
R₁₄ is H; CF₃; CN; COOR₂; Ci-Csalkyl; Ci-Csalkoxy; Ci-Csalkylthio; pyrrolidinyl; piperidinyl;
di(Ci-C₄alkyl)amino; morpholiny; phenyl; phenyl substituted by phenyl or Ci-Csalkyl or
cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio; C₂-C₅alkyl or C₃-C₁₂alkoxy or C₃-C₁₂alkylthio each of
which is interrupted by O; Ci-Csalkyl or C₂-C₁₂alkenyl or Ci-Csalkoxy or Ci-Csalkylthio each of
which is substituted by CN or COOR₂ or phenyl or fluoro or CF₃;
R₁₅ is H; CF₃; OC₃; CN; COOR₂; Ci-C₂alkyl; Ci-C₂alkoxy; Ci-C₂alkylthio; Ci-C₂alkyl-SO₂;
pyrrolidinyl; di(Ci-C₄alkyl)amino; morpholiny; phenyl; phenyl substituted by phenyl or Ci-Csalkyl
or cyclohexyl or Ci-Csalkoxy or Ci-Csalkylthio or CN or CF₃ or OCF₃; C₂-C₁₂alkyl or C₃-
Ci-C₂alkylthio each of which is interrupted by O; Ci-Csalkyl or C₂-C₁₂alkenyl or Ci-
Csalkoxy or Ci-Csalkylthio or Ci-Csalkyl-SO₂ each of which is substituted by CN or COOR₂ or
COR₂ or phenyl or fluoro or CF₃;
R₁₆ and R₁₇ independently are H, halogen, nitro, Ci-Csalkyl, Ci-Csalkoxy,
with the proviso that a compound of formula
\[
\text{R}_{21}
\]
\[
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\]
\[
\text{CH}_3
\]
, wherein R₂₁ is F, CF₃ or CN, is
excluded.
13. The composition according to claim 5, wherein the compound of formula B₁₀ conforms to
formula B₁₁, B₁₂ or B₁₃
\[
\text{Xb} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\]
(B₁₁)

\[
\text{Ar}_5 \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\]
(B₁₂)

\[
\text{Ar}_6 \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\]
(B₁₃)

wherein
q is 0 or 1;
Ar₅ is a heterocyclic residue of the formula
Ar6 is a heterocyclic residue of one of the formulae

\[ \begin{align*}
\text{wherein} \\
X_b & \text{ is } \text{Hal, COOR}_2, \text{CN, phenyl, } R_8\text{-substituted phenyl; } \\
\text{Hal} & \text{ is CF3 or fluoro; } \\
R_2 & \text{ is } \text{d-alkyl; } \\
R_5 & \text{ is } \text{Ci-Calkyl, cyclohexyl, phenyl, } \text{d-Calkyl-phenyl, Ci-Calkyl-cyclohexyl; } \\
R_{11} & \text{ is } \text{pyrrolidinyl or di(Ci-C4alkyl)amino or morpholinyl; } \\
R_{12} \text{ and } R_{13} & \text{ independently are } \text{H; Hal; CN; COOR}_2; \text{d-Calkyl; phenyl; phenyl substituted by } \\
& \text{phenyl or Ci-Calkyl or cyclohexyl or Ci-Calkoxy;} \\
& \text{C2-Calkyl or Cs-Calkylthio each of which is } \\
& \text{interrupted by O; Ci-Calkyl or vinyl each of which is substituted by CN or COOR}_2; \text{or } R_{12} \text{ and } \\
R_{13} & \text{ together are } \text{C3-Calkylene; } \\
R_{14} & \text{ is } \text{CF3; CN; COOR}_2; \text{d-Calkyl; Ci-Cgalkoxy;} \\
& \text{Ci-Cgalkylthio; pyrrolidinyl; di(Ci-C4alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or Ci-Calkyl; } \\
& \text{C2-Calkyl interrupted by O; Ci-Calkyl or vinyl or Ci-Calkylthio each of which is substituted by CN or } \\
& \text{COOR}_2 \text{ or phenyl or CF3; } \\
R_{15} & \text{ is } \text{CF3; OCF3; CN; COOR}_2; \text{d-Calkyl; Ci-Cgalkoxy;} \\
& \text{Ci-Cgalkylthio; Ci-Cgalkyl-S0}_2; \text{pyrrolidinyl; di(Ci-C4alkyl)amino; morpholinyl; phenyl; phenyl substituted by phenyl or Ci-Cgalkyl; } \\
& \text{C2-Calkyl interrupted by O; d-Calkyl or vinyl or Ci-Calkylthio or Ci-C8alkyl-S02 each of which is substituted by CN or COOR}_2 \text{ or phenyl or CF3; } \\
R_{16} \text{ and } R_{17} & \text{ independently are H, halogen, nitro.}
\end{align*} \]

14. A process for the preparation of a polarizing film or a liquid crystal display, which process comprises dissolving a dye composition according to any one of claims 1 to 9 and 13 or a compound according to claim 12 in liquid crystal material.

15. The use of a dye composition according to any one of claims 1 to 9 and 13 or a compound according to claim 12 for the preparation of a polarizing film or a liquid crystal display.

30
Fig. 1

![Graph showing absorption vs. nm with lines labeled parallel and crossed.](image-url)
### INTERNATIONAL SEARCH REPORT

#### A. CLASSIFICATION OF SUBJECT MATTER

INV. C09B31/28 C09K19/60 G02B5/30 C09B67/00 C09B31/043 C09B31/18

#### ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

- Minimum documentation searched (classification system followed by classification symbols)
  - C09B  C09K  G02B

- Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

#### Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

- EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data

#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>JP 61 133268 A (MITSUI TOATSU CHEMICALS) 20 June 1986 (1986-06-20) the whole document abstract page 454, left-hand col umn; compound 1</td>
<td>12</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

#### Date of the actual completion of the international search

27 July 2011

#### Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

#### Date of mailing of the international search report

05/09/2011

Authorized officer

Durand-Oral, 11knur

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 4 668 050 A (AOKI HISASHI [JP] ET AL)</td>
<td>1-11, 13-15</td>
</tr>
<tr>
<td></td>
<td>page 61, col umn 1 - page 65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>col umn 13 - col umn 18; examples 1-28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>col umn 18, line 58 - line 65</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>JP 59 152957 A (GOSEI SERNYO GJUTSU KENKYU KU) 31 August 1984 (1984-08-31)</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>page 378, paragraph 19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>abstract</td>
<td></td>
</tr>
<tr>
<td></td>
<td>page 383, col umn 59; compound 66</td>
<td></td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>US 4565424</td>
<td>21-01-1986</td>
<td>NONE</td>
</tr>
<tr>
<td>JP 61133268</td>
<td>20-06-1986</td>
<td>NONE</td>
</tr>
<tr>
<td>US 4668050</td>
<td>26-05-1987</td>
<td>DE 3416515 AI</td>
</tr>
<tr>
<td>JP 1463926</td>
<td></td>
<td>JP 59204659 A</td>
</tr>
<tr>
<td>JP 63009554</td>
<td></td>
<td>JP 1782159 C</td>
</tr>
</tbody>
</table>