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NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **BASF AKTIENGESELLSCHAFT** of, Carl-Bosch-Strasse 38, D-67056 Ludwigshafen, Germany being the applicant in respect of Application No. 45678/93 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors by virtue of their employment.

The person nominated for the grant of the patent is the applicant of the applications listed in the declaration under Article 8 of the PCT.

The basic applications listed on the request form are the first applications made in a Convention country in respect of the invention.

BASF AKTIENGESELLSCHAFT
By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.... 27 June 1996
Louis C. Gebhardt
Registered Patent Attorney

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(54) Title
USE OF COMPOUNDS WHICH ABSORB AND/OR FLUORESCE IN THE I/R RANGE AS MARKERS FOR LIQUIDS

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(57) Claim

1. Use of a compound from the class of metal-free or metal-containing phthalocyanines, metal-free or metal-containing naphthalocyanines, nickel dithiolene complexes, aminium compounds of aromatic amines, methine dyes or azulenesquaric acid dyes which have their absorption maximum in the range from 600 to 1,200 nm and/or a fluorescence mixture in the range from 620 to 1,200 nm, as a marker for liquids.

4. A method for detecting a marker from the class of metal-free or metal-containing naphthalocyanines, metal-free or metal-containing naphthalocyanines, nickel dithiolene complexes, aminium compounds of aromatic amines, methine dyes or azulenesquaric acid dyes which have their fluorescence maximum in the range from 620 to 1,200 nm by exciting its fluorescence and so producing fluorescent light in the NIR spectral region.

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5. A method as claimed in claim 4, wherein the fluorescence is excited by means of a semiconductor laser or a semiconductor diode.

6. A method as claimed in claim 4, wherein the fluorescence light is detected by means of a semiconductor detector.

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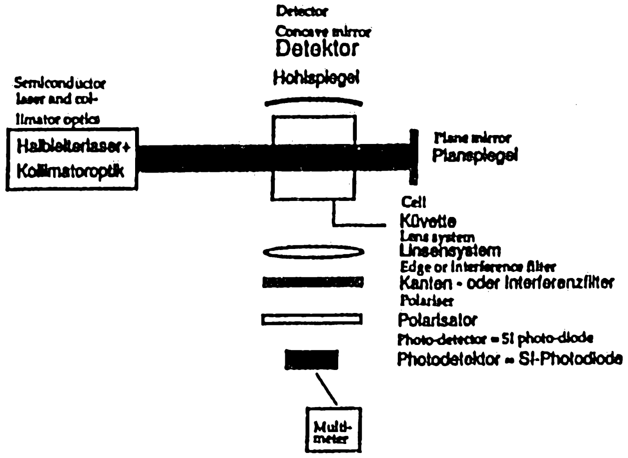
673530

(54) Title: USE OF COMPOUNDS WHICH ABSORB AND/OR FLUORESCE IN THE I/R RANGE AS MARKERS FOR LIQUIDS

(54) Bezeichnung: VERWENDUNG VON IM IR-BEREICH ABSORBIERENDEN UND/ODER FLUORESZIERENDEN VERBINDUGEN ALS MARKIERUNGSMITTEL FÜR FLÜSSIGKEITEN



(57) Abstract

The use of compounds from the class of the phtalocyanine, naphthalocyanine, nickel-dithiolene complexe, aminium compounds of aromatic amines, methine dyes or azulene quadratic acide dyes, the maximum absorption of which is in the 600 to 1,200 nm range and/or the maximum fluorescence of which is in the 620 to 1,200 nm range, as markers for liquids, a process for detecting markers in liquids and a suitable detector therefor.

(57) Zusammenfassung

Verwendung von Verbindungen aus der Klasse der Phthalocyanine, der Naphthalocyanine, der Nickel-Dithiolen-Komplexe, der Aminiumverbindungen von aromatischen Aminen, der Methinfarbstoffe oder der Azulenquadratsäurefarbstoffe, die ihr Absorptionsmaximum im Bereich von 600 bis 1 200 nm und/oder ein Fluoreszenzmaximum im Bereich von 620 bis 1 200 nm aufweisen, als Markierungsmittel für Flüssigkeiten, ein Verfahren zur Detektion von Markierungsmittel in Flüssigkeiten sowie ein dazu geeigneter Detektor.

Use of compounds which absorb and/or fluoresce in the IR region as markers for liquids

The present invention relates to the use of compounds from the class of metal-free or metal-containing phthalocyanines, metal-free or metal-containing naphthalocyanines, nickel dithiolene complexes, aminium compounds of aromatic amines, methine dyes or azulenesquaric acid dyes which have their absorption maximum in the range from 600 to 1,200 nm and/or a fluorescence maximum in the range from 620 to 1,200 nm, as markers (tracers) for liquids, to a method for detecting markers in liquids, and to a detector suitable for this purpose.

It is frequently necessary to mark liquids in order subsequently, for example when they are used, to re-detect the thus-marked liquids by means of suitable methods.

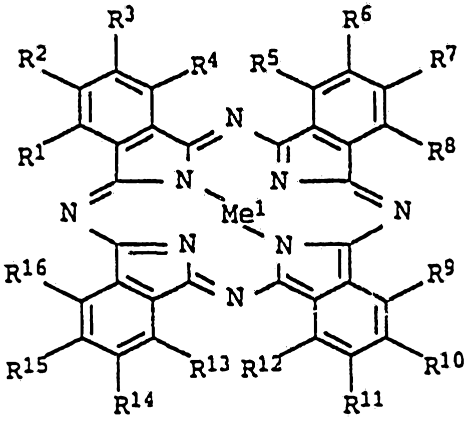
For example, heating oil can be differentiated from diesel oil in this way.

It is an object of the present invention to provide suitable compounds which are suitable as markers. The markers should have sufficiently strong absorption and/or fluorescence in the near infrared, so that detection of the absorption by means of conventional photometers which are sensitive in this range and/or of the fluorescence by means of conventional instruments after excitation with a suitable radiation source is possible.

We have found that this object is achieved by the compounds described in greater detail at the outset.

Metal-containing phthalocyanines or naphthalocynanines generally contain lithium (twice), magnesium, zinc, copper, nickel, VO, TiO or AlCl as the central atom.

Suitable phthalocyanines have, for example, the formula Ia



(Ia),

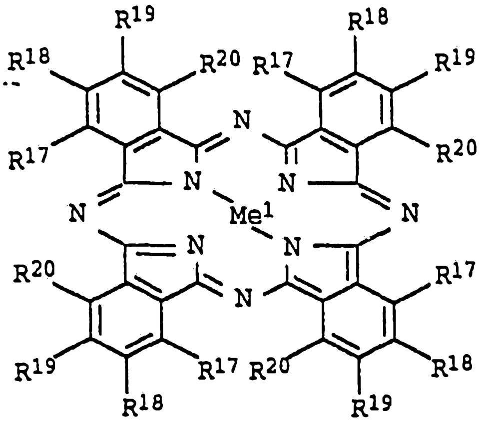
where

Me^1 is two hydrogen atoms, two lithium atoms or magnesium, zinc, copper, nickel, VO, TiO, AlCl or Si(OH)$_2$,

at least 4 of the radicals R^1 to R^{16}, independently of one another, have the formula W-X^1 in which W is a chemical bond, sulfur, imino, C$_1$-C$_4$-alkylimino or phenylimino, and X^1 is C$_1$-C$_{20}$-alkyl, which may be interrupted by from 1 to 4 oxygen atoms in ether function or substituted by phenyl, or are adamantyl or substituted or unsubstituted phenyl, and

any remaining radicals R^1 to R^{16} are hydrogen, halogen, hydroxysulfonyl or C$_1$-C$_4$-dialkylsulfamoyl.

Other suitable phthalocyanines have, for example, the formula Ib



(Ib),

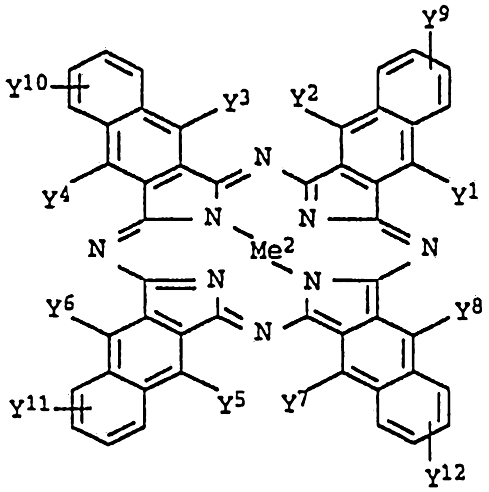
where

R^{17} and R^{18} or R^{18} and R^{19} or R^{19} and R^{20} together in each case have the formula X^2-C_2H_4-X^3, in which one of the two radicals X^2 and X^3 is oxygen and the other is imino or C_1-C_4-alkylimino, and

R^{19} and R^{20} or R^{17} and R^{20} or R^{17} and R^{18}, independently of one another, are in each case hydrogen or halogen, and

Me^1 is as defined above.

Suitable naphthalocyanines have, for example, the formula II



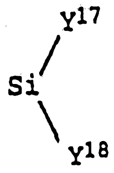
(II),

where

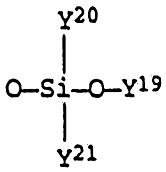
Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7 and Y^8, independently of one another, are each hydrogen, hydroxyl, C_1-C_{20}-alkyl or C_1-C_{20}-alkoxy, where the alkyl groups may each be interrupted by from 1 to 4 oxygen atoms in ether function and may be substituted by phenyl,

Y^9, Y^{10}, Y^{11} and Y^{12}, independently of one another, are each hydrogen, C_1-C_{20}-alkyl or C_1-C_{20}-alkoxy, where the alkyl groups may each be interrupted by from 1 to 4 oxygen atoms in ether function, or are halogen, hydroxysulfonyl or C_1-C_4-dialkylsulfamoyl, and

Me^2 is two hydrogen atoms, two lithium atoms, magnesium, zinc, copper, nickel, VO, TiO, AlCl or



where
Y^{17} and Y^{18}, independently of one another, are each hydroxyl, C_1-C_{20}-alkoxy, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_3-C_{20}-alkenyloxy or

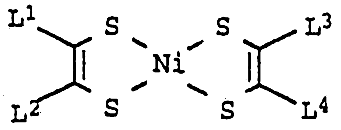


$$\text{O}-\overset{\displaystyle Y^{20}}{\underset{\displaystyle Y^{21}}{\text{Si}}}-\text{O}-Y^{19}$$

in which Y^{19} is C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl or C_4-C_{20}-alkadienyl and Y^{20} and Y^{21}, independently of one another, are each C_1-C_{12}-alkyl, C_2-C_{12}-alkenyl or as defined for OY^{19} above.

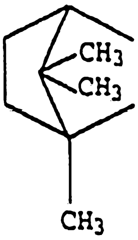
Of particular interest here are naphthalocyanines of the formula II in which at least one of Y^1 to Y^8 is not hydrogen.

Suitable nickel dithiolene complexes have, for example, the formula III

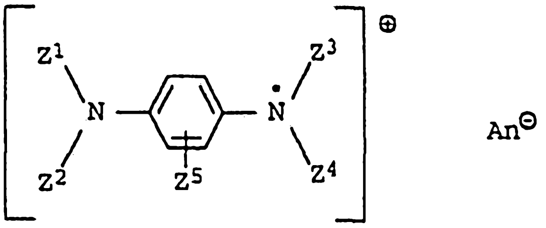


(III),

where
L^1, L^2, L^3 and L^4, independently of one another, are each C_1-C_{20}-alkyl, which may be interrupted by from 1 to 4 oxygen atoms in ether function, phenyl, C_1-C_{20}-alkylphenyl, C_1-C_{20}-alkoxyphenyl, where the alkyl groups may each be interrupted by from 1 to 4 oxygen atoms in ether function, or L^1 and L^2 and/or L^3 and L^4 in each case together are



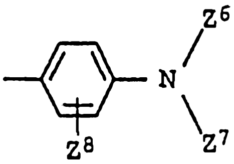
Suitable aminium compounds have, for example, the formula IV



(IV),

where

Z^1, Z^2, Z^3 and Z^4, independently of one another, are each C_1-C_{20}-alkyl, which may be interrupted by from 1 to 4 oxygen atoms in ether function, C_1-C_{20}-alkanoyl or

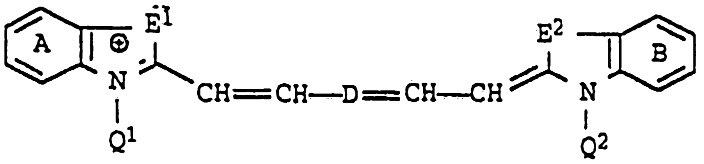


,

where Z^6 is hydrogen, C_1-C_{20}-alkyl, which may be interrupted by from 1 to 4 oxygen atoms in ether function, or C_1-C_{20}-alkanoyl, Z^7 is hydrogen or C_1-C_{20}-alkyl, which may be interrupted by from 1 to 4 oxygen atoms in ether function, and Z^8 is hydrogen, C_1-C_{20}-alkyl, which may be interrupted by from 1 to 4 oxygen atoms in ether function, or halogen, and

$An^{\ominus}$ is the equivalent of an anion.

Suitable methine dyes have, for example, the formula V



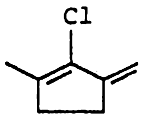
n $An^{\ominus}$ (V),

in which the rings A and B, independently of one another, may each be benzo-fused and/or substituted,

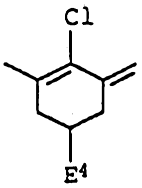
E^1 and E^2, independently of one another, are each oxygen, sulfur, imino, $-C(CH_3)_2-$ or $-CH=CH-$,

D is

$—CE^3=$ oder $—CH=CE^3—CH=$,



oder



,

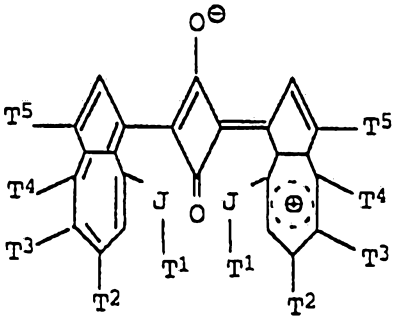
where E^3 is hydrogen, C_1-C_6-alkyl, chlorine or bromine and E^4 is hydrogen or C_1-C_6-alkyl,

Q^1 and Q^2, independently of one another, are each phenyl, C_5-C_7-cycloalkyl, C_1-C_{12}-alkyl, which may be interrupted by from 1 to 3 oxygen atoms in ether function and may be substituted by hydroxyl, chlorine, bromine, carboxyl, C_1-C_4-alkoxycarbonyl, acryloyloxy, methacryloyloxy, hydroxysulfonyl, C_1-C_7-alkanoylamino, C_1-C_6-alkylcarbamoyl, C_1-C_6-alkylcarbamoyloxy or $G^{\oplus}(K)_3$, where G is nitrogen or phosphorus and K is phenyl, C_5-C_7-cycloalkyl or C_1-C_{12}-alkyl,

$An^{\ominus}$ is the equivalent of an anion, and

n is 1, 2 or 3.

Suitable azulenesquaric acid dyes have, for example, the formula VI



(VI),

where

J is C_1-C_{12}-alkylene,

T^1 is hydrogen, halogen, amino, hydroxyl, C_1-C_{12}-alkoxy, phenyl, substituted phenyl, carboxyl, C_1-C_{12}-alkoxycarbonyl, cyano, $-NT^7-CO-T^6$, $-CO-NT^6T^7$ or $-O-CO-NT^6T^7$, where T^6 and T^7, independently of one another, are each hydrogen, C_1-C_{12}-alkyl, C_5-C_7-cycloalkyl, phenyl, 2,2,6,6-tetramethylpiperidin-4-yl or cyclohexylaminocarbonyl, and

T^2, T^3, T^4 and T^5, independently of one another, are each hydrogen or C_1-C_{12}-alkyl, which may be substituted by halogen, amino, C_1-C_{12}-alkoxy, phenyl, substituted phenyl, carboxyl, C_1-C_{12}-alkoxycarbonyl or cyano,

with the proviso that, if T^5 is hydrogen, the ring positions of the substituents $J-T^1$ and T^4 within an azulene ring may also be exchanged for one another on one or both azulene rings.

All the alkyl, alkylene and alkenyl radicals occurring in the above formulae may be either straight-chain or branched.

In the formulae Ia, II, III and IV, suitable C_1-C_{20}-alkyl radicals, which may be interrupted by from 1 to 4 oxygen atoms in ether function, are, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl, 2-methylpentyl, heptyl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl (the above terms isooctyl, isononyl, isodecyl and isotridecyl are trivial names and originate from the alcohols obtained from the oxo synthesis - cf. in this respect Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Volume 7, pages 215-217, and Volume 11, pages 435 and 436), tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2- and 3-methoxypropyl, 2- and 3-ethoxypropyl, 2- and 3-propoxypropyl, 2- and 3-butoxypropyl, 2- and 4-methoxybutyl, 2- and 4-ethoxybutyl, 2- and 4-propoxybutyl, 2- and 4-butoxybutyl, 3,6-dioxaheptyl, 3,6-dioxaoctyl, 4.8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl and 3,6,9,12-tetraoxatetradecyl.

In the formulae I and II, suitable phenyl-substituted C_1-C_{20}-alkyl radicals are, for example, benzyl and 1- and 2-phenylethyl.

In the formulae II, III and IV, suitable C_1-C_{20}-alkoxy radicals, which may be interrupted by from 1 to 4 oxygen atoms in ether function, are, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, hexyloxy, heptyloxy, octyloxy, 2-ethylhexyloxy, isooctyloxy, nonyloxy, isononyloxy, decyloxy, isodecyloxy, undecyloxy, dodecyloxy, tridecyloxy, isotridecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy, octadecyloxy, nonadecyloxy, eicosyloxy, 2-methoxyethoxy, 2-ethoxyethoxy, 2-propoxyethoxy, 2-isopropoxyethoxy, 2-butoxyethoxy, 2- and 3-methoxypropoxy, 2- and 3-ethoxypropoxy, 2- and 3-propoxypropoxy, 2- and 3-butoxypropoxy, 2- and 4-methoxybutoxy, 2- and 4-ethoxybutoxy, 2- and 4-propoxybutoxy, 2- and 4-butoxybutoxy, 3,6-dioxaheptyloxy, 3,6-dioxaoctyloxy, 4,8-dioxanonyloxy, 3,7-dioxaoctyloxy, 3,7-dioxanonyloxy, 4,7-dioxaoctyloxy, 4,7-dioxanonyloxy, 4,8-dioxadecyloxy, 3,6,8-trioxadecyloxy, 3,6,9-trioxaundecyloxy, 3,6,9,12-tetraoxatridecyloxy and 3,6,9,12-tetraoxatetradecyloxy.

In the formula II, suitable phenyl-substituted C_1-C_{20}-alkoxy radicals are, for example, benzyloxy and 1- and 2-phenylethoxy.

In the formulae Ia, III and VI, suitable substituted phenyl radicals are, for example, phenyl which is substituted by C_1-C_6-alkyl, C_1-C_6-alkoxy, hydroxyl or halogen. In general, there may be from 1 to 3 substituents.

Halogen in the formulae Ib, II, IV and VI is, for example, fluorine, chlorine or bromine.

The radicals W in the formula Ia and X^2 and X^3 in the formula Ib are, for example, methylimino, ethylimino, propylimino, isopropylimino or butylimino.

The radicals R^1 to R^{16} in the formula Ia and Y^9 to Y^{12} in the formula II are, for example, dimethylsulfamoyl, diethylsulfamoyl, dipropylsulfamoyl, dibutylsulfamoyl or N-methyl-N-ethylsulfamoyl.

C_2-C_{20}-alkenyl and C_4-C_{20}-alkandienyl in the formula II are, for example, vinyl, allyl, prop-1-en-1-yl, methallyl, ethallyl, but-3-en-1-yl, pentenyl, pentadienyl, hexadienyl, 3,7-dimethylocta-1,6-dien-1-yl, undec-10-en-1-yl, 6,10-dimethylundeca-5,9-dien-2-yl, octadec-9-en-1-yl, octadeca-9,12-dien-1-yl, 3,7,11,15-tetramethylhexadec-1-en-3-yl or eicos-9-en-1-yl.

C_3-C_{20}-alkenyloxy in the formula II is, for example, allyloxy, methallyloxy, but-3-en-1-yloxy, undec-10-en-1-yloxy, octadec-9-en-1-yloxy or eicos-9-en-1-yloxy.

Z^6 in the formula IV is, for example, formyl, acetyl, propionyl, butyryl, isobutyryl, pentanoyl, hexanoyl, heptanoyl, octanoyl or 2-ethylhexanoyl.

If the rings A and/or B in the formula V are substituted, suitable substituents are, for example, C_1-C_6-alkyl, phenyl-C_1-C_6-alkoxy, phenoxy, halogen, hydroxyl, amino, C_1-C_6-mono- or dialkylamino or cyano. The rings are generally monosubstituted to trisubstituted.

The radicals E^3, E^4, Q^1 and Q^2 in the formula V are, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, pentyl, isopentyl, neopentyl, tert-pentyl or hexyl.

The radicals Q^1 and Q^2 are furthermore, for example, hexyl, 2-methylpentyl, heptyl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, cyclopentyl, cyclohexyl, 2-methoxyethyl, 2-ethoxyethyl, 2- or 3-methoxypropyl, 2- or 3-ethoxypropyl, 2-hydroxyethyl, 2- or 3-hydroxypropyl, 2-chloroethyl, 2-bromoethyl, 2- or 3-chloropropyl, 2- or 3-bromopropyl, 2-carboxyethyl, 2- or 3-carboxypropyl, 2-methoxycarbonylethyl, 2-ethoxycarbonylethyl, 2- or 3-methoxycarbonylpropyl, 2- or 3-ethoxycarbonylpropyl, 2-acryloyloxyethyl, 2- or 3-acryloyloxypropyl, 2-methacryloyloxyethyl, 2- or 3-methacryloyloxypropyl, 2-hydroxysulfonylethyl, 2- or 3-hydroxysulfonylpropyl, 2-acetylaminoethyl, 2- or 3-acetylaminopropyl, 2-methylcarbamoylethyl, 2-ethylcarbamoylethyl, 2- or 3-methylcarbamoylpropyl, 2- or 3-ethylcarbamoylpropyl, 2-methylcarbamoyloxyethyl, 2-ethylcarbamoyloxyethyl, 2- or 3-methylcarbamoyloxypropyl, 2- or 3-ethylcarbamoyloxypropyl, 2-(trimethylammonium)ethyl, 2-(triethylammonium)ethyl, 2- or 3-(trimethylammonium)propyl, 2- or 3-(triethylammonium)propyl, 2-(triphenylphosphonium)ethyl or 2- or 3-(triphenylphosphonium)propyl.

$An^{\ominus}$ in the formulae IV and V is derived, for example, from anions of organic or inorganic acids. Particular preference is given to, for example, methanesulfonate, 4-methylbenzenesulfonate, acetate, trifluoroacetate, heptafluorobutyrate, chloride, bromide, iodide, perchlorate, tetrafluoroborate, nitrate, hexafluorophosphate and tetraphenylborate.

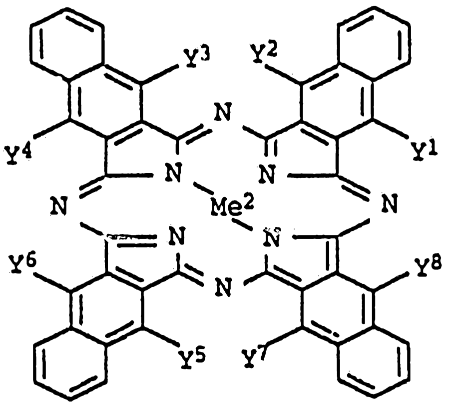
The radicals J in the formula VI are, for example, methylene, ethylene, 1,2- or 1,3-propylene, 1,2-, 1,3-, 2,3- or 1,4-butylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene, decamethylene, undecamethylene or dodecamethylene.

The radicals T^2, T^3, T^4 and T^5 in the formula VI are, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, 2-methylbutyl, hexyl, 2-methylpentyl, heptyl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, undecyl, dodecyl, fluoromethyl, chloromethyl, difluoromethyl, trifluoromethyl, trichloromethyl, 2-fluoroethyl, 2-chloroethyl, 2-bromomethyl, 1,1,1-trifluoroethyl, heptafluoropropyl, 4-chlorobutyl, 5-fluoropentyl, 6-chlorohexyl, cyanomethyl, 2-cyanoethyl, 3-cyanopropyl, 2-cyanobutyl, 4-cyanobutyl, 5-cyanopentyl, 6-cyanohexyl, 2-aminoethyl, 2-aminopropyl, 3-aminopropyl, 2-aminobutyl, 4-aminobutyl, 5-aminopentyl, 6-aminohexyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl, 4-hydroxybutyl, 5-hydroxypentyl, 6-hydroxyhexyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2-methoxypropyl, 2-ethoxypropyl, 3-ethoxypropyl, 4-ethoxybutyl, 4-isopropoxybutyl, 5-ethoxypentyl, 6-methoxyhexyl, benzyl, 1-phenylethyl, 2-phenylethyl, 4-chlorobenzyl, 4-methoxybenzyl, 2-(4-methylphenyl)ethyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl, 5-carboxypentyl, 6-carboxyhexyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, 2-methoxycarbonylethyl, 2-ethoxycarbonylethyl, 3-methoxycarbonylpropyl, 3-ethoxycarbonylpropyl, 4-methoxycarbonylbutyl, 4-ethoxycarbonylbutyl, 5-methoxycarbonylpentyl, 5-ethoxycarbonylpentyl, 6-methoxycarbonylhexyl or 6-ethoxycarbonylhexyl.

T^1 in the formula VI is, for example, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, butoxycarbonyl, isobutoxycarbonyl, sec-butoxycarbonyl, tert-butoxycarbonyl, pentoxycarbonyl, isopentoxycarbonyl, neopentoxycarbonyl, tert-pentoxycarbonyl, hexyloxycarbonyl, heptyloxycarbonyl, octyloxycarbonyl, isooctyloxycarbonyl, nonyloxycarbonyl, isononyloxycarbonyl, decyloxycarbonyl, isodecyloxycarbonyl, undecyloxycarbonyl, dodecyloxycarbonyl, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, hexyloxy, acetylamino, carbamoyl, mono- or dimethylcarbamoyl, mono- or diethylcarbamoyl, monocyclohexylcarbonyl, phenylcarbamoyl, dimethylcarbamoyloxy or diethylcarbamoyloxy.

Preference is given to the use according to the invention of compounds originating from the class of metal-free or metal-containing naphthalocyanines.

Emphasis should be placed on the use according to the invention of naphthalocyanines of the formula IIa

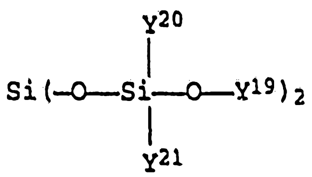


(IIa),

where

Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7 and Y^8, independently of one another, are each hydrogen, hydroxyl, C_1-C_4-alkyl or C_1-C_{20}-alkoxy, and

Me^2 is two hydrogen atoms, two lithium atoms, magnesium, zinc, copper, nickel, VO, AlCl or



$$\mathrm{Si}(-\mathrm{O}-\underset{\displaystyle Y^{21}}{\overset{\displaystyle Y^{20}}{\mathrm{Si}}}-\mathrm{O}-Y^{19})_2$$

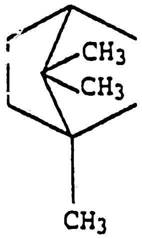
where R^{19} is C_1-C_{13}-alkyl or C_{10}-C_{20}-alkadienyl and Y^{20} and Y^{21}, independently of one another, are each C_1-C_{13}-alkyl or

C_2-C_4-alkenyl.

Particular emphasis should be placed on the use according to the invention of naphthalocyanines of the formula IIa, where Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7 and Y^8, independently of one another, are each hydroxyl or C_1-C_{20}-alkoxy, in particular C_1-C_{10}-alkoxy. The alkoxy radicals here may be identical or different.

Particular emphasis should furthermore be placed on the use according to the invention of naphthalocyanines of the formula IIa where Me^2 is two hydrogen atoms.

Emphasis should furthermore be placed on the use according to the invention of nickel dithiolene complexes of the formula III, where L^1, L^2, L^3 and L^4, independently of one another, are each phenyl, C_1-C_{20}-alkylphenyl, C_1-C_{20}-alkoxyphenyl or hydroxyl- and C_1-C_{20}-alkyl substituted phenyl, or L^1 and L^2 and L^3 and L^4 are in each case together



Particular emphasis should furthermore be placed on the use according to the invention of nickel dithiolene complexes of the formula III where L^1 and L^4 are each phenyl and L^2 and L^4 are each 4-[C_2H_5-C(CH_3)$_2$]-C_6H_4.

The phthalocyanines of the formula Ia are known per se and are described, for example, in DE-B-1 073 739 or EP-A-155 780 or can be obtained by methods known per se, as used in the preparation of phthalocyanines or naphthalocyanines and as described, for example, in F.H. Moser, A.L. Thomas, "The Phthalocyanines", CRC Press, Boca Rota, Florida, 1983, or J. Am. Chem. Soc. 106 (1984), 7404 to 7410. The phthalocyanines of the formula

Ib are likewise known per se and are described, for example, in EP-A-155 780 or can be obtained by the above prior-art methods (Moser, J. Am. Chem. Soc.).

The naphthalocyanines of the formula II are likewise known per se and are described, for example, in EP-A-336 213, EP-A-358 080, GB-A-2,168,372 or GB-A-2,200,650, or can be obtained by the above prior-art methods (Moser, J. Am. Chem. Soc.).

The nickel dithiolene complexes of the formula III are likewise known per se and are described, for example, in EP-A-192 215.

The aminium compounds of the formula IV are likewise known per se and are described, for example, in US-A-3,484,467 or can be obtained by the methods mentioned therein.

The methine dyes of the formula V are likewise known per se and are described, for example, in EP-A-464 543 or can be obtained by the methods described therein.

The azulenesquaric acid dyes of the formula VI are likewise known per se and are described, for example, in EP-A-310 080 or US-A-4,990,649 or can be obtained by the methods described therein.

Suitable solvents which can be marked according to the invention by means of the compounds described in greater detail above are, in particular, organic liquids, for example alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, pentanol, isopentanol, neopentanol and hexanol, glycols, such as 1,2-ethylene glycol, 1,2- and 1,3-propylene glycol, 1,2-, 2,3- and 1,4-butylene glycol, di- and triethylene glycol and di- and tripropylene glycol, ethers, such as methyl tert-butyl ether, 1,2-ethylene glycol mono- and dimethyl ether, 1,2-ethylene glycol mono- and diethyl ether, 3-methoxypropanol, 3-isopropoxypropanol, tetrahydrofuran and dioxane, ketones, such as acetone, methyl ethyl ketone and diacetone alcohol, esters, such as methyl acetate, ethyl acetate, propyl acetate and butyl acetate, aliphatic and aromatic hydrocarbons, such as pentane, hexane, heptane, octane, isooctane, petroleum ether, toluene, xylene, ethylbenzene, tetralin, decalin, dimethylnaphthalene, white spirit, mineral oil, such as gasoline, kerosene, diesel oil and heating oil, natural oils, such as olive oil, soya oil and sunflower oil, and natural or synthetic engine oils, hydraulic oils and transmission oils, for example vehicle engine oil and sewing machine oil, and brake fluids.

The abovementioned compounds are particularly advantageously used for marking mineral oils in which labeling is simultaneously required, for example for tax reasons. In order to keep costs of the labeling low, the usual aim is to use very dilutable dyes for the coloring. However, even dyes of high tinctorial strength cannot be detected purely visually in high dilution in mineral oils.

For this reason, it is of particular advantage to use markers which have their absorption maximum in the range from 600 to 1,200 nm and/or fluoresce in the range from 620 to 1,200 nm, since they can easily be detected using suitable instruments.

For labeling liquids, but in particular mineral oil, the abovementioned compounds are generally used in the form of solutions. Suitable solvents are preferably aromatic hydrocarbons, such as toluene and xylene. In order to avoid any excessively high viscosity of the resultant solutions, a concentration of the compound which absorbs and/or fluoresces in the IR of from 2 to 50 % by weight, based on the solution, is generally selected.

The present invention furthermore provides a process for detecting markers in liquids, which comprises detecting the marker from its fluorescence in the NIR (near infrared) spectral region.

The fluorescence of the markers present in the liquids is advantageously excited by means of a semiconductor laser or a semiconductor diode. It is particularly favorable to use a semiconductor laser or a semiconductor diode having a wavelength of maximum emission in the spectral range from λ_{max}-100 nm to λ_{max}+20 nm, where λ_{max} is the wavelength of the absorption maximum of the marker. The wavelength of maximum emission is in the range from 620 to 1,200 nm.

The fluorescence light produced in this way is advantageously detected by means of a semiconductor detector, in particular a silicon photodiode or a germanium photodiode.

Detection is particularly advantageous if the detector is preceded by an interference filter and/or a cut-off filter (with a short-wave transmission cut-off limit in the range from λ_{max} to λ_{max}+80 nm) and/or a polarizer.

The abovementioned compounds make it very simple to detect marked liquids, even if the marker substances are only present in a concentration of approximately 0.1 ppm (detection by absorption) or approximately 5 ppb (detection by fluorescence).

The present invention furthermore provides an instrument for carrying out the process according to the invention (= detector), the detector comprising an NIR light source (semiconductor laser or semiconductor diode), one or more optical filters, an NIR polarizer and a photodetector (silicon photodiode or germanium photodiode) and, if desired, optical fibers or optical fiber bundles.

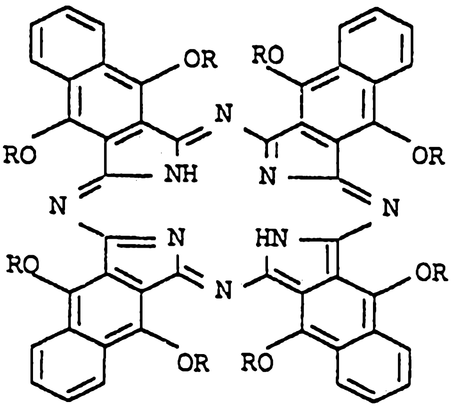
The examples below are intended to illustrate the invention in greater detail.

General procedure for detecting the markers.

I. Detection by absorption in the IR region

EXAMPLE 1

Sufficient dye of the formula



$R=n\text{-}C_4H_9$

was dissolved in diesel fuel to give a solution containing 1,000 ppm of dye.

This solution was diluted further in steps, and its absorption in the NIR region measured against a pure diesel fuel using a commercially available spectrometer (1 cm cell).

Dye content in diesel fuel [ppm]	Absorption	Absorption maximum [nm]
100	>> 3	-
50	3.05	844.0
20	2.81	854.0
10	2.10	860.4
1	0.27	860.0

Similarly favorable results are achieved when naphthalocyanines of the above formula (where $R = n\text{-}C_5H_{11}$ or $n\text{-}C_{12}H_{25}$) or the dyes listed below are used for the marking.

Dye 2

Hexadecaphenylthiocopper phthalocyanine

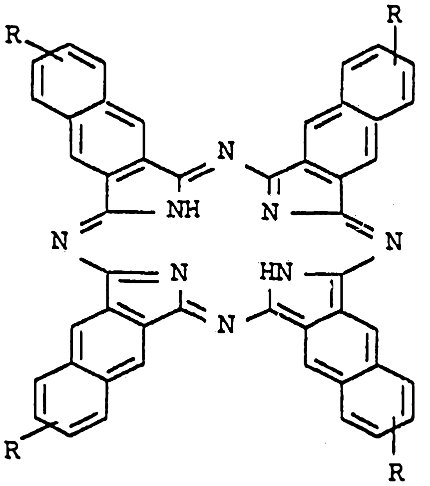
Dye 3

Tetradecaphenylthiocopper phtahlocyanine

Dye 4

Tetradecadodecylthiocopper phthalocyanine

Dye 5



$(R = t\text{-}C_4H_9)$

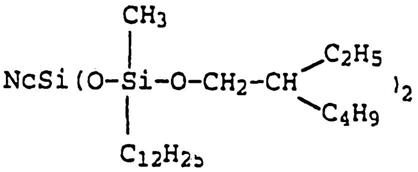
Dye 6

Hexadeca(4-tert-butylphenylthio)copper phthalocyanine

Dye 7

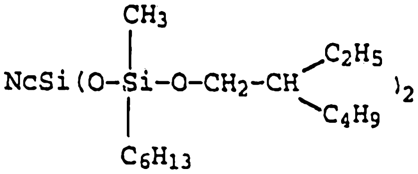
$NcSi[\text{-}O\text{-}Si(CH_3)_2\text{-}O\text{-}C_{12}H_{25}]_2$

Dye 8



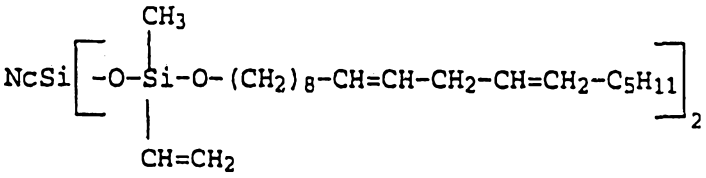
$$NcSi\left(O\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle C_{12}H_{25}}{Si}}\text{-}O\text{-}CH_2\text{-}CH\begin{matrix}C_2H_5\\C_4H_9\end{matrix}\right)_2$$

Dye 9



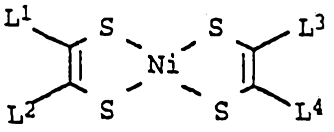
$$NcSi\left(O\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_{13}}{Si}}\text{-}O\text{-}CH_2\text{-}CH\begin{matrix}C_2H_5\\C_4H_9\end{matrix}\right)_2$$

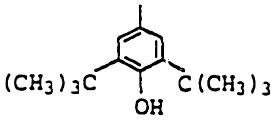
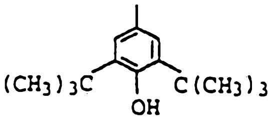
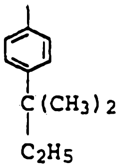
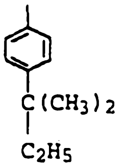
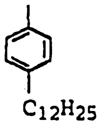
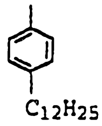
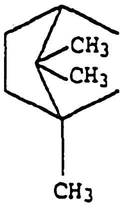
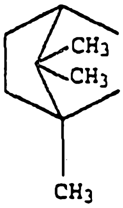
Dye 10



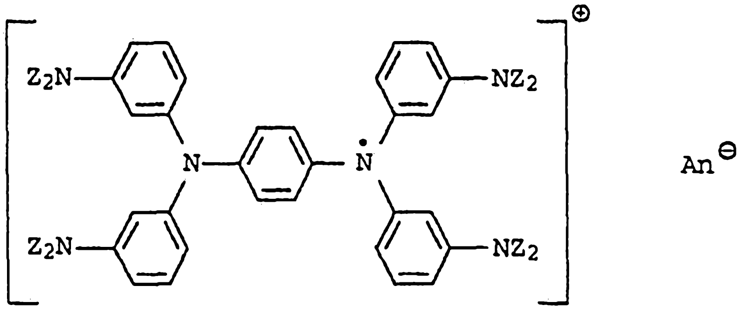
$$\mathrm{NcSi}\left[-\mathrm{O}-\underset{\mathrm{CH=CH_2}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-(\mathrm{CH_2})_8-\mathrm{CH=CH-CH_2-CH=CH_2-C_5H_{11}}\right]_2$$

Dyes 11 to 15



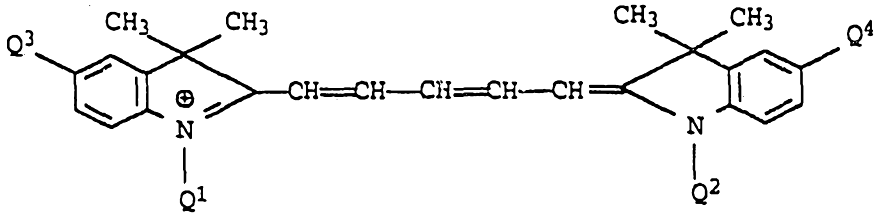
Farbstoff-Nr.	L^1	L^2	L^3	L^4
11		C_6H_5		C_6H_5
12		C_6H_5		C_6H_5
13	C_6H_5	C_6H_5	C_6H_5	C_6H_5
14		C_6H_5		C_6H_5
15				

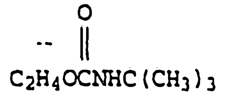
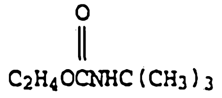
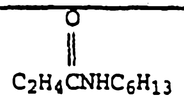
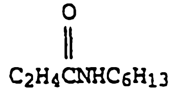
Dyes 15 to 18



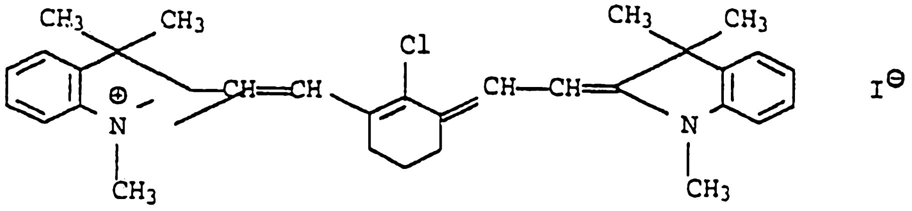
Farbstoff Nr.	Z	An$^{\ominus}$
16	C_4H_9	$NO_3^{\ominus}$
17	C_2H_5	$NO_3^{\ominus}$
18	C_4H_9	$BF_4^{\ominus}$

Dyes 19 to 23



Farbstoff Nr.	Q^1	Q^2	Q^3	Q^4	An$^{\ominus}$
19	CH_3	CH_3	Cl	Cl	$I^{\ominus}$
20	CH_3	CH_3	H	H	$I^{\ominus}$
21	 $C_2H_4O\overset{O}{\overset{\|}{C}}NHC(CH_3)_3$	 $C_2H_4O\overset{O}{\overset{\|}{C}}NHC(CH_3)_3$	H	H	$I^{\ominus}$
22	 $C_2H_4\overset{O}{\overset{\|}{C}}NHC_6H_{13}$	 $C_2H_4\overset{O}{\overset{\|}{C}}NHC_6H_{13}$	H	H	$ClO_4^{\ominus}$
23	$C_3H_6SO_3^{\ominus}$	$C_3H_6SO_3H$	H	H	Betain

Dye 24



II. Detection by fluorescence in the NIR region

Figure 1 shows the diagrammatic structure of the detector.

The marker fluorescence is excited using the emission from a commercial semiconductor diode laser. The parallel laser beam is shone onto the sample in a 1 cm cell. In order to double the excitation intensity, the transmitted light beam is reflected by a mirror and again shone through the sample.

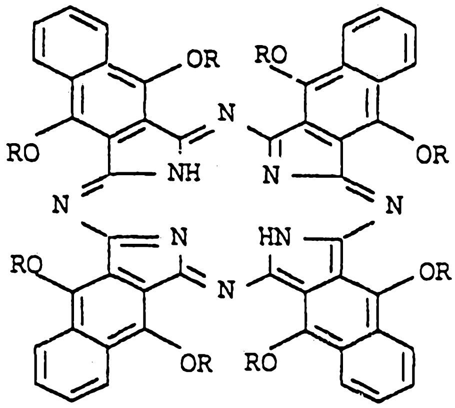
The fluorescence light is imaged by means of optical elements (lens system) onto the detector, a silicon photodiode. The light emitted at the rear is likewise thrown onto the silicon photodiode by a concave mirror.

In order to separate the unwanted light (scattered excitation light) from the fluorescence light, cutoff and/or interference filters and/or a polarizer (NIR polarization foil) are used.

The optimization of the polarizer is selected so that the direction of maximum transmission is perpendicular to the polarization plane of the excitation light.

Example 25

Sufficient dye of the formula



R=n-C_4H_9

was dissolved in diesel fuel to give a stock solution containing 219 ppb of dye. Further solutions were prepared therefrom by dilution with diesel fuel.

These solutions were measured in accordance with general procedure II using the following equipment settings.

Excitation: GaAlAs semiconductor diode laser having a wavelength of 813 nm; CW output 7 mW.

Filter: Long-pass interference filter 850 nm (Corion).

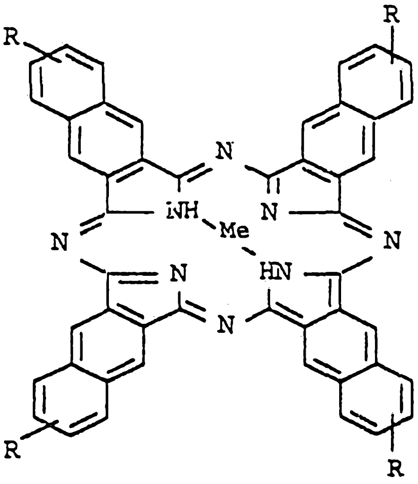
Photodetector: Silicon photodiode having an area of 1 cm^2 (UDT). The photocurrent was measured using a current/voltage converter (UDT, model 350).

The results are shown in the table below.

Dye content in the diesel fuel [ppb]	Absorbance at λ_{max}	Fluorescence signal (in scale units)
219	0.05	2366
43.7	0.01	451
8.75	0.002	106
1.75	0.0004	40
0	0.0	20

This gives a lower detection limit for the marker by fluorescence of about 5 ppb.

Similarly favorable results are achieved when naphthalocyanines of the above formula (where R = n-C_5H_{11} or n-$C_{12}H_{25}$) or the dyes listed below are used for the marking.



(R=t-C_4H_9)

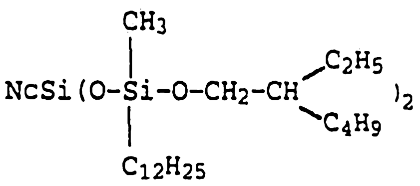
Dye 26
Me = 2H

Dye 27
Me = Zn

Dye 28
Me = AlCl

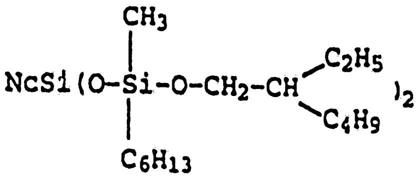
Dye 29
$NcSi[-O-Si(CH_3)_2-O-C_{12}H_{25}]_2$

Dye 30



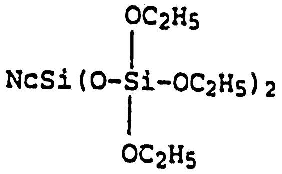
$$NcSi(O-\underset{C_{12}H_{25}}{\overset{CH_3}{Si}}-O-CH_2-CH\begin{matrix}C_2H_5\\C_4H_9\end{matrix})_2$$

Dye 31



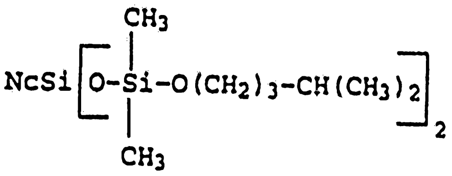
$$\mathrm{NcSi(O{-}\underset{C_6H_{13}}{\overset{CH_3}{Si}}{-}O{-}CH_2{-}CH\genfrac{}{}{0pt}{}{C_2H_5}{C_4H_9})_2}$$

Dye 32



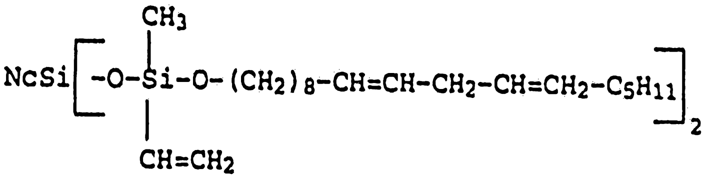
$$\mathrm{NcSi(O{-}\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}{-}OC_2H_5)_2}$$

Dye 33



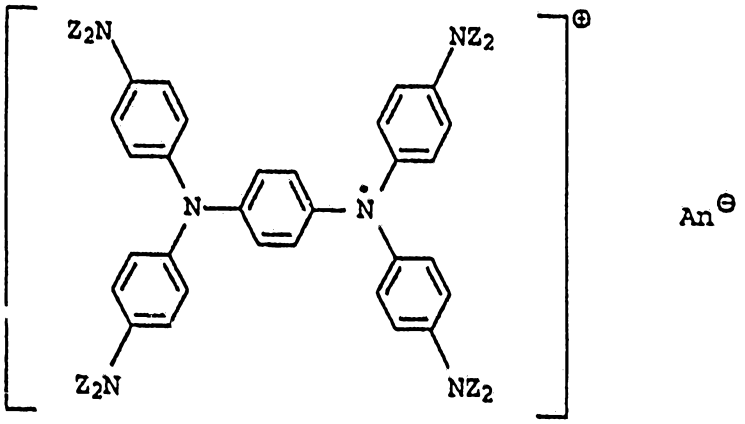
$$\mathrm{NcSi\left[O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O(CH_2)_3{-}CH(CH_3)_2\right]_2}$$

Dye 34



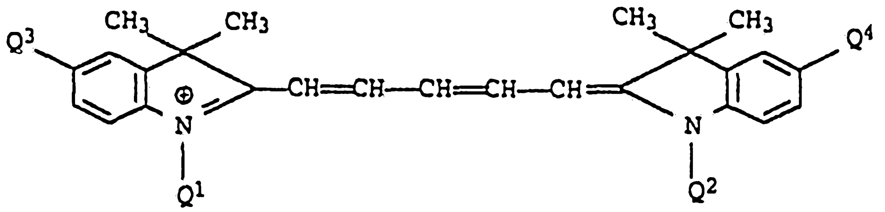
$$\mathrm{NcSi\left[{-}O{-}\underset{CH{=}CH_2}{\overset{CH_3}{Si}}{-}O{-}(CH_2)_8{-}CH{=}CH{-}CH_2{-}CH{=}CH_2{-}C_5H_{11}\right]_2}$$

Dyes 35 to 37



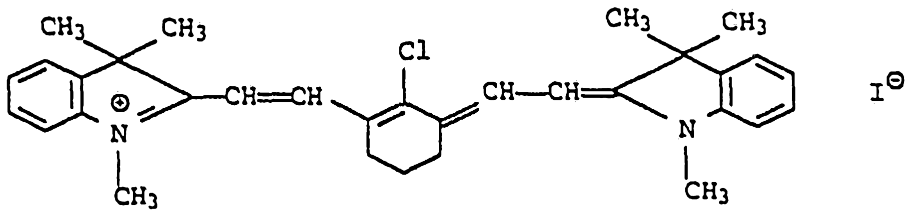
Dye No.	Z	An$^\ominus$
35	C_4H_9	$NO_3^\ominus$
36	C_2H_5	$NO_3^\ominus$
37	C_4H_9	$BF_4^\ominus$

Dyes 38 to 42



Farbstoff Nr.	Q^1	Q^2	Q^3	Q^4	An$^\ominus$
38	CH_3	CH_3	Cl	Cl	$I^\ominus$
39	CH_3	CH_3	H	H	$I^\ominus$
40	$C_2H_4O\overset{O}{\overset{\|}{C}}NHC(CH_3)_3$	$C_2H_4O\overset{O}{\overset{\|}{C}}NHC(CH_3)_3$	H	H	$I^\ominus$
41	$C_2H_4\overset{O}{\overset{\|}{C}}NHC_6H_{13}$	$C_2H_4\overset{O}{\overset{\|}{C}}NHC_6H_{13}$	H	H	$ClO_4^\ominus$
42	$C_3H_6SO_3^\ominus$	$C_3H_6SO_3H$	H	H	Betain

Dye 43



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Use of a compound from the class of metal-free or metal-containing phthalocyanines, metal-free or metal-containing naphthalocyanines, nickel dithiolene complexes, aminium compounds of aromatic amines, methine dyes or azulenesquaric acid dyes which have their absorption maximum in the range from 600 to 1,200 nm and/or a fluorescence mixture in the range from 620 to 1,200 nm, as a marker for liquids.

2. A use as claimed in claim 1, wherein the compounds comes from the class of metal-free or metal-containing naphthalocyanines or nickel dithiolene complexes.

3. A use as claimed in claim 1, wherein the compound comes from the class of metal-free or metal-containing naphthalocyanines.

4. A method for detecting a marker from the class of metal-free or metal-containing naphthalocyanines, metal-free or metal-containing naphthalocyanines, nickel dithiolene complexes, aminium compounds of aromatic amines, methine dyes or azulenesquaric acid dyes which have their fluorescence maximum in the range from 620 to 1,200 nm by exciting its fluorescence and so producing fluorescent light in the NIR spectral region.

5. A method as claimed in claim 4, wherein the fluorescence is excited by means of a semiconductor laser or a semiconductor diode.

6. A method as claimed in claim 4, wherein the fluorescence light is detected by means of a semiconductor detector.

7. A method as claimed in claim 4, wherein a semiconductor laser or a semiconductor diode having a wavelength of maximum emission in the spectral range from λ_{max}-100 nm to λ_{max}+20 nm is used, where λ_{max} is the wavelength of the absorption maximum of the marker.

8. A method as claimed in claim 4, wherein a semiconductor laser or a semiconductor diode having a wavelength of maximum emission of from 620 to 1,200 nm is used.

DATED this 27 day of June, 1996
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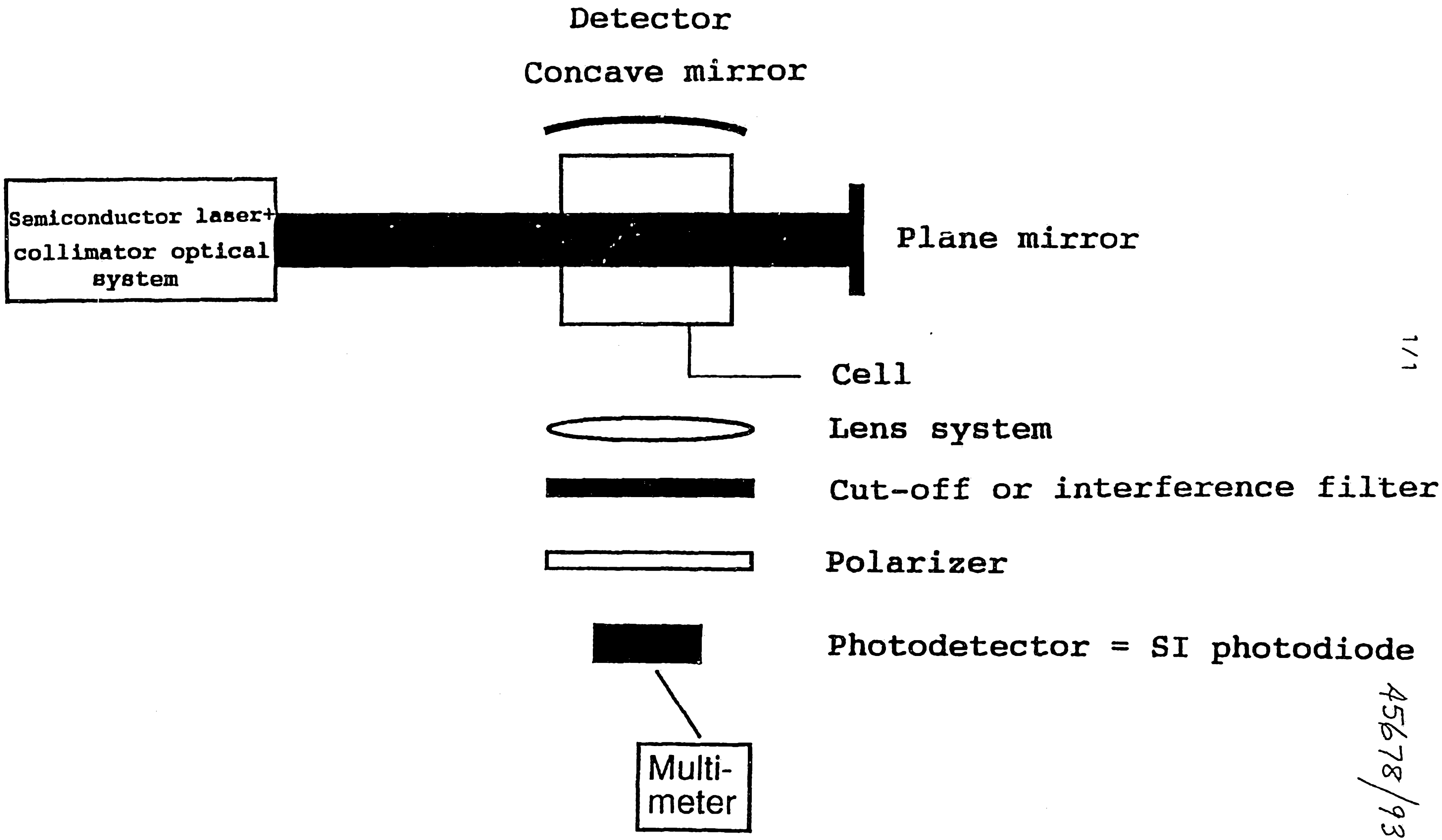
LCG/JGC/SH DOC 7 AU4567893.WPC


Detector
Concave mirror
Semiconductor laser+ collimator optical system
Plane mirror
Cell
Lens system
Cut-off or interference filter
Polarizer
Photodetector = SI photodiode
Multi-meter

45678/93

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 93/01830

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.^5 C10L 1/10

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)

Int.Cl.^5 C10L

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4209302 (ORELUP, R.B.) 24 June 1980 (24.06.80) claim 1	1-3
A	US, A, 4009008 (ORELUP, R.B.) 22 February 1977 (22.02.77) abstract	1
A	US, A, 4735631 (ORELUP, R.B.) 5 April 1988 (05.04.88) abstract	1
A	EP, A2, 0155780 (IMPERIAL CHEMICAL INDUSTRIES PLC) 25 September 1985 (25.09.85) claim 1	1-3
A	EP, A2, 0358080 (BASF AKTIENGESELLSCHAFT) 14 March 1990 (14.03.90) claim 1	1-3
A	EP, A1, 0192215 (BASF AKTIENGESELLSCHAFT) 27 August 1986 (27.08.86) claim 1	1
A	US, A, 3484467 (SUSI, P.V. ET AL.) 16 December 1969 (16.12.69) claim 1	1
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☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

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"E" earlier document but published on or after the international filing date

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"&" document member of the same patent family

Date of the actual completion of the international search 21 September 1993 (21.09.93)	Date of mailing of the international search report 29 October 1993 (29.10.93)
Name and mailing address of the ISA/ EUROPEAN PATENT OFFICE Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 93/01830

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0464543 (BASF AKTIENGESELLSCHAFT) 8 January 1992 (08.01.92) claim 1 --	1
A	EP, A2, 0310080 (BASF AKTIENGESELLSCHAFT) 5 April 1989 (05.04.89) claim 1 ------------	1

SA 5759

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/08/93

International application No.
PCT/EP 93/01830

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CH-A,B- 648587	29/03/85
		DE-A,C- 3017653	29/01/81
		FR-A,B- 2456322	05/12/80
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		NL-A- 8002708	12/11/80
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		JP-C- 1085216	25/02/82
		JP-C- 1146254	12/05/83
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		JP-B- 57036940	06/08/82
		LU-A- 68949	05/07/74
		NL-A- 7315382	11/06/74
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		US-A- 4049393	20/09/77
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		JP-A- 1110562	27/04/89
		US-A- 5084592	28/01/92
		DE-A- 3816187	23/11/89

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/EP 93/01830

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES

IPC5: C10L 1/10
Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)

IPC5: C10L

Recherte, aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

WPI, CLAIMS/US PATENT ABS, JAPIO, CA SEARCH

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichning der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	US, A, 4209302 (ORELUP, R.B.), 24 Juni 1980 (24.06.80), Anspruch 1 --	1-3
A	US, A, 4009008 (ORELUP, R.B.), 22 Februar 1977 (22.02.77), Zusammenfassung --	1
A	US, A, 4735631 (ORELUP, R.B.), 5 April 1988 (05.04.88), Zusammenfassung --	1
A	EP, A2, 0155780 (IMPERIAL CHEMICAL INDUSTRIES PLC), 25 September 1985 (25.09.85), Anspruch 1 --	1-3

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen.

☒ Siehe Anhang Patentfamilie.

* Besondere Kategorien von angegebenen Veröffentlichungen:

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"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche 21 September 1993	Absendedatum des internationalen Recherchenberichts 29. 10. 93
Name und Postanschrift der Internationalen Recherchenbehörde Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bevollmächtigter Bediensteter INGA-KARIN PETERSSON

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/EP 93/01830

C (Fortsetzung). ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	EP, A2, 0358080 (BASF AKTIENGESELLSCHAFT), 14 März 1990 (14.03.90), Anspruch 1 --	1-3
A	EP, A1, 0192215 (BASF AKTIENGESELLSCHAFT), 27 August 1986 (27.08.86), Anspruch 1 --	1
A	US, A, 3484467 (SUSI, P.V. ET AL.), 16 Dezember 1969 (16.12.69), Anspruch 1 --	1
A	EP, A1, 0464543 (BASF AKTIENGESELLSCHAFT), 8 Januar 1992 (08.01.92), Anspruch 1 --	1
A	EP, A2, 0310080 (BASF AKTIENGESELLSCHAFT), 5 April 1989 (05.04.89), Anspruch 1 -- --------	1

S/ '6759

INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

26/08/93

Internationales Aktenzeichen
PCT/EP 93/01830

Im Recherchenbericht angefurtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
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		DE-A,C- 3017653	29/01/81
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		CH-A- 606306	31/10/78
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		FR-A,B- 2212390	26/07/74
		GB-A- 1394018	14/05/75
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		JP-A- 4252268	08/09/92
EP-A2- 0310080	05/04/89	DE-A- 3733173	20/04/89
		JP-A- 1110562	27/04/89
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