



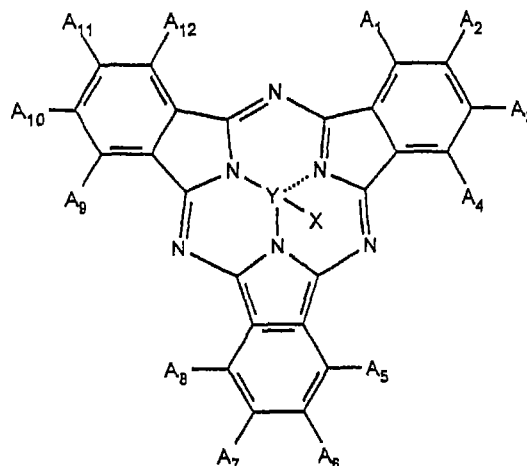
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OPTICAL RECORDING MEDIUM AND METHOD FOR MANUFACTURING IT

The invention lies in the field of optical data storage means and relates to an optical recording medium according to the preamble of the first independent claim and to a method for manufacturing the optical recording medium according to the preamble of the corresponding independent claim.

Known optical data storage means comprise a disk-like substrate of a transparent plastic, a recording layer deposited on the substrate and a reflecting layer deposited on the recording layer. The substrate comprises on the one side on which the recording layer is deposited a spiral-shaped recording groove. Data are stored by writing along this groove with a laser beam serving writing beam, wherein the recording layer is locally changed and bubble like pits are formed between the recording layer and the substrate. A further laser beam serving as reading beam scans the written track, wherein the reflection of the reading beam on the reflecting layer is recorded as a read signal.

Optical data storage means of the type DVD-R (digital versatile disc recordable) differ from optical data storage means of the type CD-R (compact disc recordable) in that the recording grooves lie closer to one another and that the disks usually comprise two substrate halves, between which the recording layer and the reflecting layer are arranged. For writing and reading DVD-Rs, laser beams with a wavelength of 630 to 680 nm are used (CD-R: 780nm). Suitable recording layers consist of a recording medium which, for absorbing the laser energy contains e.g. subphthalocyanine-boron compounds of the following general formula:



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wherein A1 to A12 independently of one another are -H, -halogen, -alkyl, -aryl, -alkyl-aryl, -oxi-alkyl, -oxi-aryl, -oxi-alkyl-aryl, -thio-alkyl, -thio-aryl or -thio-alkyl-aryl, wherein the alkyl groups have 1 to 20 carbon atoms and the aryl groups are phenyl or naphthyl groups or their halogen derivatives, and wherein Y is boron.

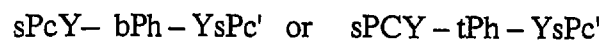
X is, as for example described in the publication US-5776656, a halogen, -OH, -OC₂H₅ or -O-tert.-butyl. In the same publication it is suggested that X is a phenyl or phenoxy group which preferably is not substituted.

The recording layer further contains in a known manner a quencher, for example in the form of a metal complex (e.g. metal-thiolene complex) and where appropriate a stabilizer, for example an amine.

It is the object of the invention to provide a recording medium for optical data storage means being readable and writable with a laser of a wavelength between 630 and 680 nm (e.g. DVD-R), said recording medium being based on a subphthalocyanine and to be distinguished from known such recording mediums by a particularly high stability against light and climatic influences and by way of the fact that a recording layer of the recording medium according to the invention may be written with a very high speed (particularly low optimal write energy). Furthermore it is the object of the invention to create a method for manufacturing the recording medium.

These objects are achieved by the recording medium and the method for its manufacture as defined in the claims.

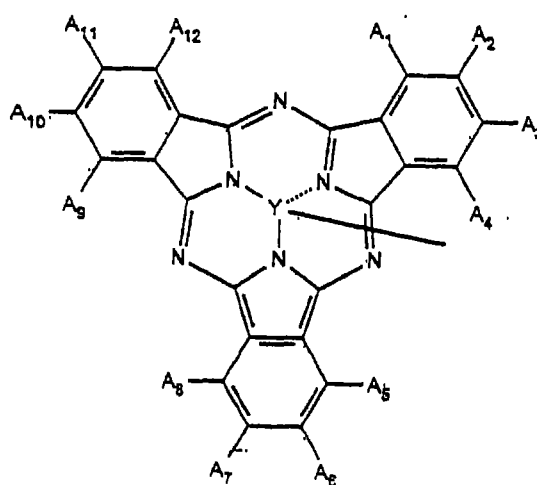
The recording medium according to the invention contains as a laser energy absorbing compound a subphthalocyanine with boron or aluminium as a central atom. This subphthalocyanine in the recording medium according to the invention is present in the form of ion complexes and specifically partly as an ion complex which consists of two or three subphthalocyanine units (sPcY-) and a bis- or triphenolate or a bis- or tris thiophenolate (-bPh- or >tPh-) ion, and partly as an ion complex which consists of a subphthalocyanine unit (sPcY-) and an anionic metal thiolene complex or metal diazo complex (MC). The recording medium according to the invention thus contains the following ion complexes:



and $\text{sPcY}''' - \text{MC}$

wherein:

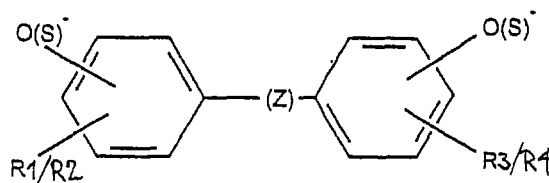
sPcY , sPcY' , sPcY'' and sPcY''' are equal or different subphthalocyanines and have the following general structure:



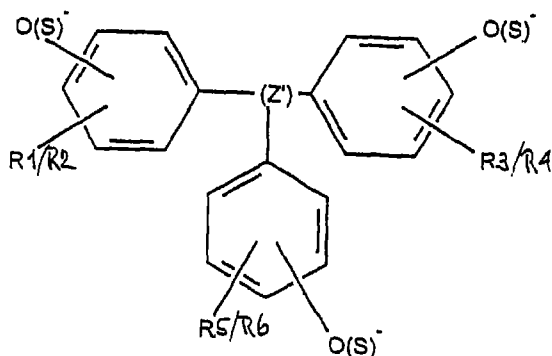
wherein A1 to A12 independently of one another are -H, -halogen, -alkyl, -aryl, -alkyl-aryl, -oxi-alkyl, -oxi-aryl, oxi-alkyl-aryl, -thio-alkyl, -thio-aryl or -thio-alkyl-aryl, wherein the alkyl groups have 1 to 20 carbon atoms and the aryl groups are phenyl or naphthyl groups or halogen-substituted derivatives thereof, and wherein Y is boron or aluminum;

wherein bPh and tPh have the following, general structures:

bPh:

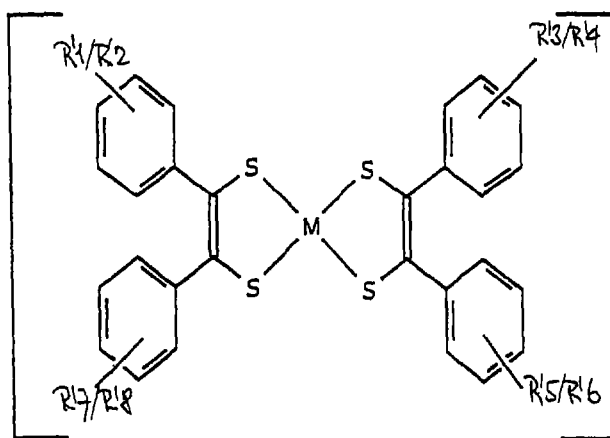
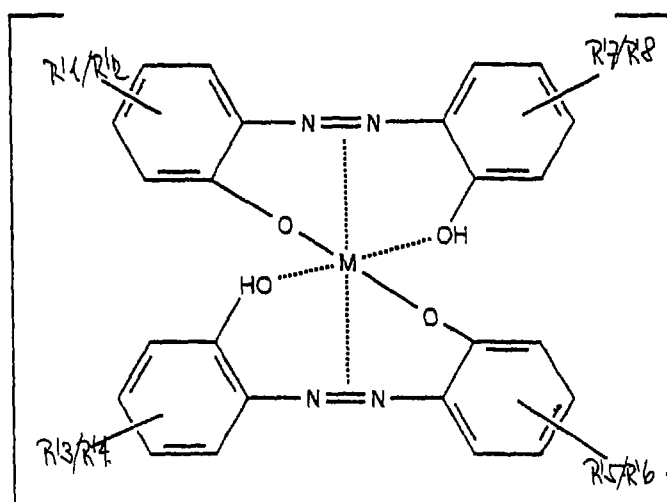


tPh:



wherein at the location of Z there is nothing, $-\text{CH}_2-$, $-\text{C}_2\text{H}_4-$, $-\text{S}-$, $-\text{O}-$ or $-\text{NH}-$ and at the location of Z' there is $-(\text{C}_n\text{H}_{(2n-1)})<$ with $n = 1, 2$ or 3 or $-\text{N}<$ and wherein each benzene ring additionally to the $-\text{O}^-$ or $-\text{S}^-$ group carries up to two further substituents R1 to R6, wherein R1 to R6 independently of one another are -halogen, -CN, -NO, -alkyl, -aryl, -alkyl-aryl, -oxi-alkyl, -oxi-aryl, -oxi-alkyl-aryl, -thio-alkyl, -thio-aryl, -thio-alkyl-aryl, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{H}$, $-\text{SO}_3\text{N}(\text{alkyl})_2$, $-\text{NH}_2$, $-\text{NH}(\text{alkyl})$, $-\text{NH}(\text{aryl})$, $-\text{N}(\text{alkyl})_2$, $-\text{N}(\text{aryl})_2$, wherein the alkyl groups comprise 1 to 8 carbon atoms and the aryl groups are -phenyl or -naphthyl or substituted derivatives thereof;

wherein MC is a metal thiolene complex or a metal diazo complex of the following general structure:



wherein M = Ni, Co, Fe, Cu, Sn, Zn, Al, Ti, TiO, Cr, V, VO, Pt, Pd, Ge or Si and wherein each benzene ring carries up to two substituents R'1 to R'8, wherein R'1 to R'8 independently of one another is -halogen, -NO₂, -NH₂, -NH(alkyl), -NH(aryl), N(alkyl)₂, N(aryl)₂, -CN, -oxi-alkyl, oxi-aryl, -thio-alkyl, -thio-aryl, wherein the alkyl groups have 1 to 8 carbon atoms and the aryl groups are -phenyl or -naphthyl or substituted derivatives thereof.

The subphthalocyanine units present in the recording medium according to the invention may all be equally substituted and have the same central atoms Y (boron or aluminum) or they may be substituted differently and have different central atoms Y. Advantageously in all subphthalocyanine units the substituents A1 to A4 are equal to the substituents A5 to A8 and equal to the substituents A9 to A12.

Preferred examples of subphthalocyanines have the following substituents:

A1 to A12 = -H (unsubstituted sPcY);

A1, A4, A5, A8, A9, A12 = -octyl and A2, A3, A6, A7, A10, A11 = -H;

A2, A3, A6, A7, A10, A11 = -octyl and A1, A4, A5, A8, A9, A12 = -H;

A2 or A3, A6 or A7, A10 or A11 = -S-octyl and all others = -H

A2, A6, A10 = -phenoxy and all others = -H;

A1, A5, A9 = -thiophenoxy and all others = -H

A1, A5, A9 = -oxi-hexyl, A3, A7, A11 = -Cl

Of the bis- or trisphenolates or the bis- or trithiophenolates in the recording medium according to the invention one may be present or a mixture of various such phenolates. At the same time in each of the phenolates the substituents R1/R2 are advantageously the same as the substituents R3/R4 and R5/R6.

Preferred examples of bis- and trisphenolates or -thiophenolates are the anions of the following phenols:

2,2'-methylene-bis(6-tert.-butyl-4-methylphenol),

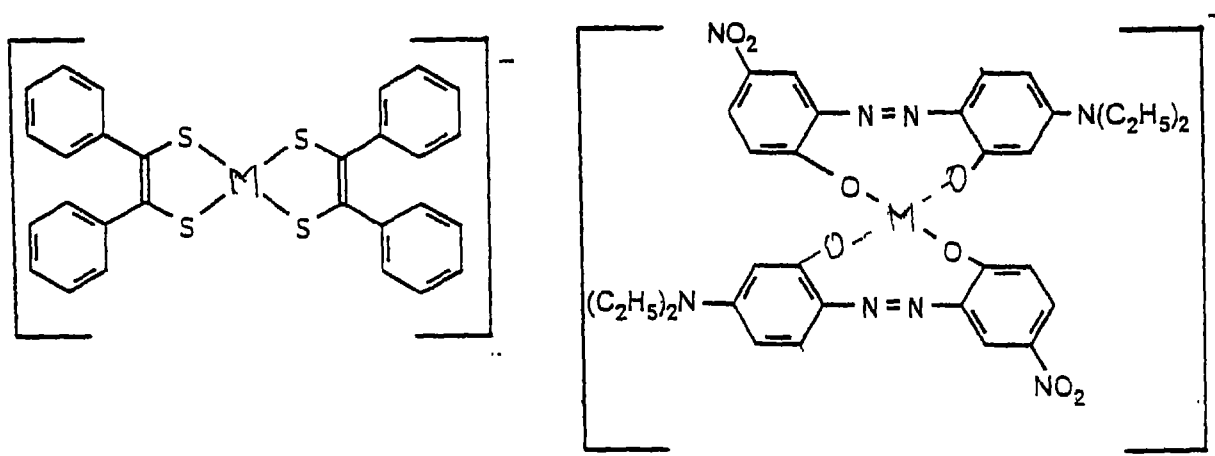
2,2'-methylene-bis(6-tert.-butyl-4-ethylphenol),

2,2'-methylene-bis(4,6-dimethylphenol),

2,2'-isobutylidene-bis(4,6-dimethylphenol),

2,2'-methylene-bis(4-methyl-6- α -cyclohexylphenol),
 4,4-methylene-bis(2,6-di-tert.-butylphenol),
 4,4-butyldiene-bis(6-tert.-butyl-3-methylphenol),
 2,2'-thio-bis(6-ter.-butyl-4-methylphenol),
 2,2'-thio-bis(4-methyl-6- α -methylbenzylphenol),
 2,2'-thio-bis(4,6-di-sek.-amylphenol),
 4,4'-thio-bis(6-tert.-butyl-2-methylphenol),
 bis-(4-hydroxy-3,5-di-tert.-butylbenzyl)-sulphide,
 2,2'-bis(5-diethylamino-phenol),
 4,4'-diethyl-6,6'-ditert.-butyl-2,2'-bisphenol,
 4,4'-diethyl-6,6'-di-tert-butyl-2,2'-bis-thiophenol,
 1,1,3-tris(5'-tert.-butyl-4'-hydroxy-2'-methylphenyl)-butane.

Preferred anionic metal thiolene complexes and metal diazo complexes are the following:



The mole ratio between the ion complex (sPcY)₂-bPh or (sPcY)₃-tPh (ion complex of subphthalocyanine and bis- or tris-phenolate or - thiophenolate) and the ion complex sPcY-MC (ion complex of subphthalocyanine and anionic metal thiolene complex or metal diazo complex) is between 1:99 to 99:1.

The recording medium may contain cyanine, styryl, formazan, diazo and/or metalised diazo dyes as further laser energy absorbing compounds in addition to the phthalocyanine ion complexes. Furthermore, it may contain metallocenes (e.g. ferrocene), acetyl acetonate metal complexes, N,N'-tetra-alkyl- (or -aryl)-substituted paradiamino benzenes and/or chinoline with

weight portions of up to 10 parts for 100 parts of the laser energy absorbing compound or compounds.

The subphthalocyanines with boron or aluminum as a central atom are manufactured in that a suitably substituted 1,2-dicyano-benzene (phthalonitril) is reacted with boron or aluminum halogenide (advantageously boron or aluminum chloride). 1,8-diazabicyclo [5.4.0]-7-undecene (DBU) used as a catalyst (advantageously with a mole ratio to the phthalonitrils of 0.1:2 to 1:2). This reaction produces a subphthalocyanine halogenide.

The subphthalocyanine halogenide is then separately on the one hand dissolved with an excess of bis- or trisphenolate and on the other hand with an excess of anionic metal thiolene complex or metal diazo complex (advantageously in an approx. five-fold excess) in a suitable organic solvent or solvent mixture and at an increased temperature is stirred for a longer time (e.g. at 60-100°C for 5 to 50 hours).

Then the water-soluble salts are washed out with water and the organic ion complexes are isolated, washed, purified by recrystallisation or in another suitable manner, and dried.

For producing the recording layer, the separately manufactured subphthalocyanine ion complexes of the recording medium are dissolved in the desired ratio where appropriate together with the further compounds in an organic solvent. The solution of the recording medium is for example deposited onto the substrate of polycarbonate by spin coating and then is dried. On the recording medium created in this manner, a reflecting layer of silver, gold or aluminum or of an alloy of these metals is deposited for example by way of sputtering. This is, where appropriate, covered with a protective varnish layer and the disk created in this manner is fixed to a second substrate having also a protective varnish layer by way of an adhesive layer.

Example 1: synthesis of an unsubstituted subphthalocyanine-boron compound

Dried 1,2-dicyanobenzene (0.5g, 0.04mol) was suspended under nitrogen together with DBU (0.02 moles) in freshly distilled chlorobenzene (12ml). The suspension was cooled to -3°C and from an injection syringe, 20.5 ml of a 1-molar solution of boron chloride (BCl₃) in n-hexane was added slowly. The yellow-green solid body was slowly and with strong stirring heated to

60°C, wherein the fluid became black. The hexane was distilled off. Then stirring was continued at 100°C for a further 10 minutes. The color changed to violet. The liquid phase was removed and the solid body was firstly extracted with petrol ether (80°C-100°C) and then for two hours with toluol. The remaining brown solid body was recrystallized from ethanol, washed with petrol ether and sublimed at 350°C. The result was 3.57g (64%) of a brown, powder-like product: UV(DMF) λ_{max} : 562, 302nm; IR (KBr): 1692, 1611, 1452, 1384, 1280, 1195, 1130, 950, 878, 753, 695, 629 cm^{-1} ; ^1H NMR (360 MHz) (DMSO- d_6): δ 8.85 (6H, dd), 7.90 (6H dd); MS (EI 70 eV, 260°C): m/z 464 ($\text{M}^+ + \text{Cl-H}$, 4), 431 (M^+ , 20), 430, (55), 429 (18), 396 (70), 267 (10), 256 (8), 215 (5), 197.5 (35), 139 (15).

Example 2: Synthesis of a trithioocetyl-substituted subphthalocyanine aluminum compound (mixture of regio-isomeres)

Dried 4-thio-phthalonitrile (460g, 1.79mmol) and DBU (1mmol) were suspended in 0.5 ml chloro-benzene under argon. Through a cannula, 0.15ml (1,79) mol of aluminum chloride (previously condensed at -78°C) was added using a slight argon excess pressure. The mixture was then stirred at room temperature for 10 minutes, then for 15 min at 80°C. After cooling, the precipitated black solid body was washed with hexane, filtered and chromatographed with hexane/methylene chloride (1:1) on Al_2O_3 . This resulted in 201g (44%) of a sticky violet compound.

Example 3: Manufacture of an ion complex of subphthalocyanine and biphenolate

To a 5% solution of 0.01mol 1,4,5,8,9,12-hexa-octyl-sPc-boron bromide in n-butanol a five-fold excess with respect to molar mass of the sodium salt of 4,4'-diethyl-6,6'-ditert.-buty-2,2'-bisphenol was added. The obtained solution was stirred for 12 hours at 80°C, cooled and subsequently poured into cold water wherein organic constituents precipitated and the water-soluble inorganic salts were dissolved. The precipitated solid body was filtered off, washed with water, recrystallized from ethanol and dried in a vacuum.

Example 4: Manufacture of an ion complex of subphthalocyanine and bithiophenolate.

To a 5% solution of 0.01 mols of 2,6,10-triphenoxy-sPc-boron bromide in chloro-benzene a five-fold excess in relation to the subphthalocyanine of the sodium salt of 4,4'-diethyl-6,6'-di-tert-butyl-2,2'-bis-thiophenol was added. The obtained solution was stirred for 10 hours at 80°C. Thereafter the solvent was distilled off and then the product was recrystallized from ethanol and dried in a vacuum.

Example 5: Manufacture of an ion complex of subphthalocyanine and metal diazo complex

To a 5% solution of 0.01 mol 1,5,9-tri-thiophenoxy-sPc-boron(III)-bromide in dimethyl formamide/H₂O (95:5), bis-(2-hydroxi-5-nitro-4'-diethylamino-diazo-phenol)-TiO(II)-tetra-butyl ammonium bromide was added. The obtained solution was stirred for 12 hours at 70°C, cooled and poured into cold water. Thereafter the procedure was the same as described in example 3.

Example 6: Manufacture of an ion complex of subphthalocyanine and metal dithiolene complex

To a 5% solution of 0.01mol 1,5,9-trihexyl-oxy-3,7,11-trichloro-sPc-boron(III)-bromide in dimethylformamide/H₂O (95:5), bis-1,2(4-methoxybenzol-1,2-dithiolene)-Ni(II)-tetra-butyl ammonium bromide was added. The obtained solution was stirred for 15 hours at 70°C, cooled and then poured into cold water. Thereafter the procedure was the same as described in example 3.

Example 7: Manufacture and testing of optical data storage means

The ion complexes containing subphthalocyanine obtained in the examples 3 to 6 were used for manufacturing DVD-R data storage means.

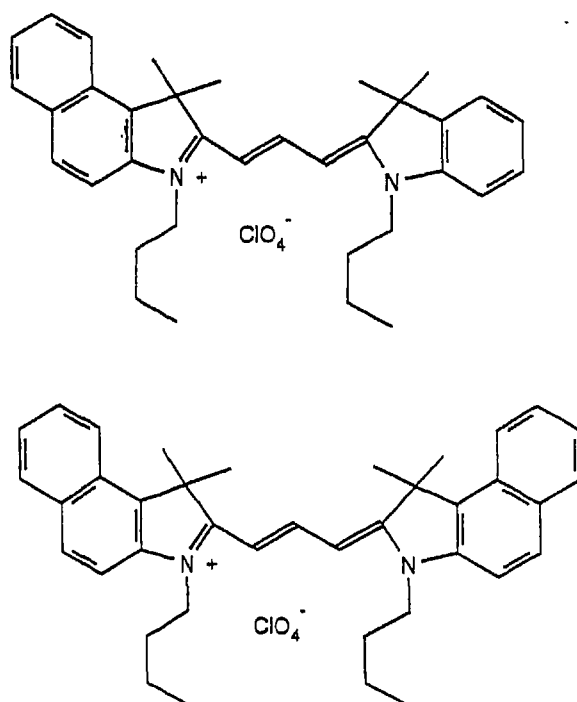
The separately manufactured, purified and dried subphthalocyanine-containing ion complexes and, where appropriate, further compounds were dissolved under stirring in an

organic solvent or solvent mixture (e.g. 2,2,3,3-tetrafluoropropanol, 2-ethoxyethanol, diazotone alcohol/butanol (10:1), diazotone alcohol/isopropanol (10:1) or ethylcellosolve) in the desired quantity ratios. The concentration of the solutions was varied in the region of 0.5 - 5% (weight).

The necessary substrate disks of polycarbonate were manufactured by injection molding (diameter 120 mm, thickness 0.6 mm). The discs comprised on one surface a groove spiral with a pitch of $0.74\mu\text{m}$. Depending on the used recording medium, groove depths in the region of 100-200nm and groove widths in the region of 180-400nm were selected. The recording layers were deposited by spin coating. Depending on the optical parameters of the laser energy absorbing compounds in the recording medium, the thickness of the recording layers in the grooves were varied in the range of 90-140nm and on the lands in the range of 10-30nm.

The coated polycarbonate substrates were subsequently dried at 70 to 80°C. By way of sputtering, a reflecting gold layer with a layer thickness of 70-120nm was deposited. Subsequently a protective varnish layer (thickness approx. $4\mu\text{m}$) was deposited and cured under UV irradiation. Polycarbonate disks without dye or metal layers were likewise provided with a protective varnish layer. In each case one disk with a recording, metal and protective varnish layer and one disk with only a protective varnish layer were adhesively joined to one another using a suitable adhesive.

As a standard data storage means, disks with a recording layer of the trimethinecyanine dyes of the company Fuji Foto Film Co. Ltd were manufactured in the same manner, the dyes having the following structures:



The recording layer of the standard disks further comprised a quencher (Q), e.g. IRG 22 of the company Nippon Kayako Co. Ltd..

The disks manufactured in the manner as described above were written and tested using a test apparatus of the company e-focus with a laser beam (wavelength 635nm; linear writing speed: 3.49m/s). Then they were tested for light and environment stability (according to the ISO-105-B02 standard using air-cooled xenon lamps and according to JEC68-2-2Ba and JEC68-2-30Dd).

All data storage means comprising a recording layer of a recording medium according to invention fulfill the standards, also after the light and climate tests.

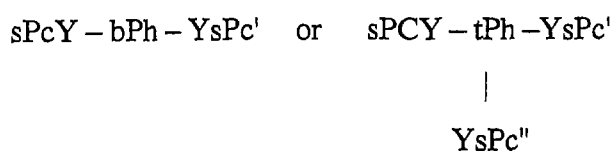
In subsequent table, the test results are summarized as mean values in comparison to the state of the art (best value according to US-6168843, TDK Corporation and standard disks with a recording medium based on methine dyes).

The optical data storage means comprising a recording layer of a recording medium according to the invention may successfully write and read with a laser beam with a wavelength of 650nm, wherein also here the standard parameters are achieved. A computer simulation indicates that the optical data memories with a recording layer of recording medium according to the invention may also be written with writing speeds larger than 4x.

Recording medium	opt. write-energy (mW)	modulation (%)	refle. (%)	jitter (%)
Accord. US 6,168,843 (TDK Corporation)	7.2	60	46	8.0
70%C1 + 20%C2 + 10%Q	>12	---	---	---
(sPcY) ₂ -bPh or (sPcY) ₃ -tPh(1)	7.2	60	50	8.0
sPcY-m thiolene c. (2)	7.0	64	48	7.9
sPcY-m diazo c. (3)	6.9	68	47	7.8
15%(1) + 85% (2)	6.7	70	48	7.6
5% (1) + 95% (3)	6.4	71	47	7.5
10% (1) + 30%(2) + 60% (3)	6.4	71	48	7.5
30%C1 + 10%(1) + 20%(2) + 40% (3)	6.2	72	46	7.4
standard	6<OSE<12	≥60	>45	<8,0

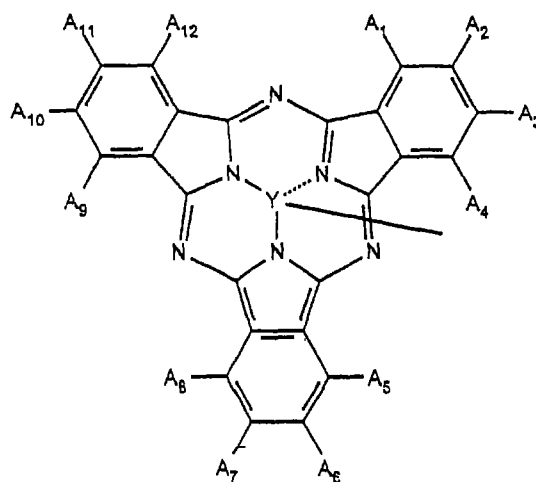
CLAIMS

1. A recording medium for an optical data storage means writable and readable with a laser beam of a wavelength of 630 to 680nm, said recording medium for the absorption of the laser energy containing a subphthalocyanine (sPcY) present partly as an ion complex with a bis- or trisphenolate or a bis- or trithiophenolate (bPh or tPh) and partly as an ion complex with an anionic metal thiolene complex or metal diazo complex (MC), said ion complexes having the following structures:



and $\text{sPcY}''' - \text{MC}$

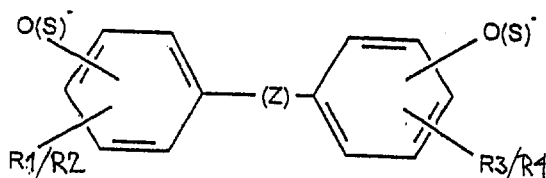
wherein sPcY-, sPcY'-, sPcY''- and sPcY'''- are equal or different and have the following structure:



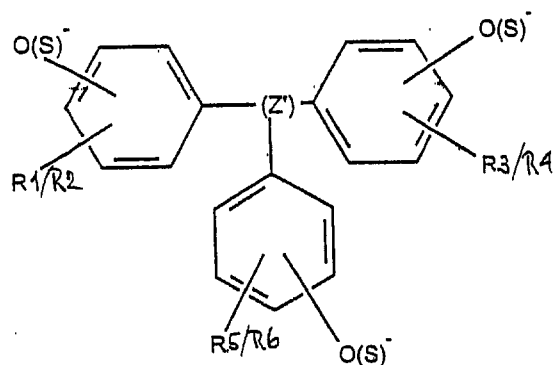
wherein A1 to A12 independently of one another are -H, -halogen, -alkyl, -aryl, -alkyl-aryl, -oxi-alkyl, -oxi-aryl, -oxi-alkyl-aryl, -thio-alkyl, -thio-aryl or -thio-alkyl-aryl, wherein said alkyl groups have 1 to 20 carbon atoms and said aryl groups are -phenyl or -naphthyl groups or halogen substituted derivatives thereof, and wherein Y is boron or aluminum;

wherein bPh and tPh have the following, general structures:

bPh:

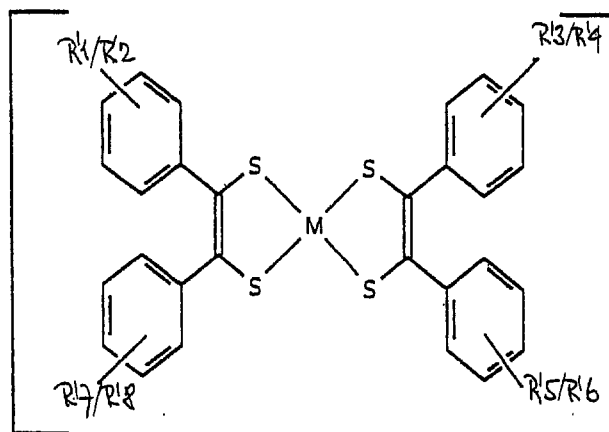


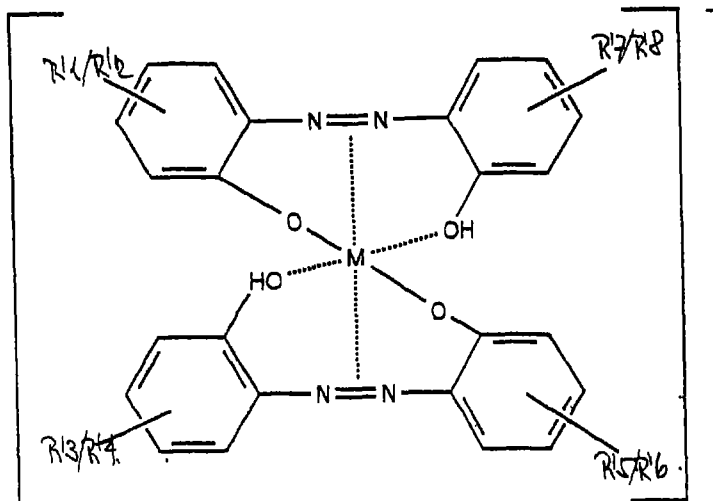
tPh:



wherein at the location of Z there is nothing, $-\text{CH}_2-$, $-\text{C}_2\text{H}_4-$, $-\text{S}-$, $-\text{O}-$ or $-\text{NH}-$ and at the location of Z' there is $-(\text{C}_n\text{H}_{(2n-1)})_<$ with $n = 1, 2$ or 3 or $-\text{N}<$ and wherein each benzene ring in addition to the $-\text{O}^-$ or $-\text{S}^-$ group carries up to two further substituents R1 to R6 which independently of one another are -halogen, -CN, $-\text{NO}_2$, -alkyl, -aryl, -alkyl-aryl, -oxi-alkyl, -oxi-aryl, -oxi-alkyl-aryl, -thio-alkyl, -thio-aryl, -thio-alkyl-aryl, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{H}$, $-\text{SO}_3\text{N}(\text{alkyl})_2$, $-\text{NH}_2$, $-\text{NH}(\text{alkyl})$, $-\text{NH}(\text{aryl})$, $-\text{N}(\text{alkyl})_2$, $-\text{N}(\text{aryl})_2$, wherein said alkyl groups comprise 1 to 8 carbon atoms and said aryl groups are -phenyl or -naphthyl or substituted derivatives thereof;

wherein MC is a metal thiolene complex or a metal diazo complex of the following general structure:





wherein M = Ni, Co, Fe, Cu, Sn, Zn, Al, Ti, TiO, Cr, V, VO, Pt, Pd, Ge or Si and wherein each benzene ring carries up to two substituents R'1 to R'8, wherein R'1 to R'8 independently of one another are -halogen, -NO₂, -NH₂, -NH(alkyl), -NH(aryl), -N(alkyl)₂, -N(aryl)₂, -CN, -oxi-alkyl, -oxi-aryl, -thio-alkyl, -thio-aryl and wherein the mentioned alkyl groups have 1 to 8 carbon atoms and the mentioned aryl groups are -phenyl or -naphthyl or substituted derivatives thereof.

2. The recording medium according to claim 1, characterized in that the mole ratio of the ion complex comprising the bis- or tris-phenolate or -thiophenolate and the ion complex comprising the anionic metal thiolene complex or the metal diazo complex lies between 1:99 and 99:1.

3. The recording medium according to one of claims 1 or 2, characterized in that the subphthalocyanines at least partly have equal substituents A1, A4, A5, A8, A9 and A12 and equal A2, A3, A6, A7, A10 and A11.

4. The recording medium according to one of claims 1 to 3, characterized in that in the bis- or tris-phenolate or -thiophenolate the substituents R1 and R2 are the same as the substituents R3 and R4 and the same as the substituents R5 and R6.

5. The recording medium according to one of claims 1 to 4, characterized in that in the metal thiolene complexes or metal diazo complexes the substituents R1, R3, R5 and R7 are all the same and the substituents R2, R4, R6 and R8 are all the same.

6. The recording medium according to one of claims 1 to 4, characterized in that in the metal thiolene complexes or metal diazo complexes, of the substituents are the same in the following manner: $R1/R2 = R7/R8$ and $R3/R4 = R5/R6$.
7. The recording medium according to one of claims 1 to 6, characterized in that it contains in addition to the subphthalocyanine at least one further compound absorbing laser energy.
8. The recording medium according to claim 7, characterized in that the further laser energy absorbing compound is a cyanine dye, a styryl dye, a formazane dye, a diazo dye or a metallized diazo dye.
9. The recording medium according to one of claims 1 to 8, characterized in that it further contains a metallocene, an acetyl acetonate metal complex, an N,N'-tetra-substituted paradiamino phenol and/or chinoline.
10. A data storage means of the DVD-R type with a substrate of transparent plastic, with a reflecting layer and with a recording layer being arranged between the substrate and the reflecting layer, characterized in that the recording layer consists of a recording medium according to one of the claims 1 to 9.
11. The data storage means according to claim 10, characterized in that on a side of the reflecting layer facing away from the recording layer, a second layer of a transparent plastic is provided.
12. The data storage means according to claim 11, characterized in that the reflecting layer and the second plastic layer each carries a protective varnish layer, the protective varnish layers being joined to one another with an adhesive.
13. The data storage means according to one of claims 10 to 12, characterized in that the reflecting layer consists of gold, silver, aluminum or of a gold, silver or aluminum alloy.

14. A method for manufacturing a recording medium according to one of the claims 1 to 12, characterized in that the ion complexes of the recording medium are individually synthesized purified and dried and that they are then dissolved in the desired quantity ratios in an organic solvent.
15. The method according to claim 14, characterized in that the ion complexes are synthesized by reacting a subphthalocyanine halogenide with an excess of the bis- or tris-phenolate or -thiophenolate or of the metal thiolene complex or the metal diazo complex.
16. The method according to claim 15, characterized in that the excess is a fivefold molar excess.
17. The method according to one of claims 15 or 16, characterized in that the ion complexes are synthesized by stirring reactant mixtures at temperatures of 60-100°C for 5 to 50 hours.
18. The method according to one of claims 15 to 17, characterized in that the subphthalocyanine halogenide is synthesized by reacting phthalonitriles with boron halogenide or aluminum halogenide in the presence of 1,8 diazabicyclo [5.4.0]-7-undecene (DBU).
19. The method according to claim 18, characterized in that DBU is applied in a molar ratio to the phthalonitrils of 0.1:2 to 1:2.