Use of Cu phthalocyanine sulfonammonium amides as dyes for write-once optical data stores

The present invention provides a write-once optical data carrier using Cu phthalocyanine sulfonammonium amides as dyes, in particular for CD-Rs, and also application of the dyes mentioned above to a polymer substrate (in particular polycarbonate) by spin-coating.

Write-once compact disks (CD-Rs) have recently experienced enormous volume growth accompanied by a simultaneous drop in price. The main component in the manufacturing cost is the information-carrying dye. The prior art comprises the use of expensive cyanine, phthalocyanine and azo dye systems which are synthesised specifically for the spectral requirements and the solubility required.

In the patent literature, the necessity for using such expensive modified phthalocyanine dyes is based e.g. on the following arguments:

- Specific substituents prevent the formation of dye associates in thin films. Associates adversely alter the absorption spectrum for applications as optical data stores (US 5124067).
- Specific substituents prevent crystallisation of the dyes in thin films. Crystallites adversely alter the layer homogeneity for application as optical data stores (EP-A2-519419).
- Only specific substituents enable solubility of the generally sparingly soluble phthalocyanines in those solvents which do not interfere with the groove structure of the injection moulded plastic substrate when spin-coating on a plastics substrate (mainly polycarbonate) (US 5124067).
- Central atoms with a large atomic radius (Pd, Pt, Rh, Ru, In, VO) have to be used in order to achieve the highest possible refractive index at the write and

read wavelengths (780 - 820 nm), which guarantees a high signal modulation for application as CD-Rs (EP-A1-0513370).

- Specific substituents and central atoms enable a high molar absorption (>200000). This high molar absorption is required for sufficiently high modulation of the read signal for the CD-R specification (US 5124067).
- Patent EP-A1-519395 (Eastman Kodak Co.) describes metal phthalocyanine dyes with certain sulfonamide groups ($SO_2NR^1R^2$) for write-once optical data stores.
- Patent JP-A-05177946 (Taiyo Yuden) describes sulfonamide derivatives of a zinc phthalocyanine dye as the information layer for optical data stores. The dye is intended to be soluble in alcohol and Cellosolve.

These types of highly specialised dye systems are expensive and therefore prevent the cost-effective production of e.g. write-once compact discs (CD-Rs).

Accordingly, the object of the invention is the provision of a simple to synthesise phthalocyanine dye which complies with the high requirements (such as light stability, favourable signal-to-noise ratio, application to a substrate material without causing damage, etc.) for use as the information layer in a write-once optical data carrier (primarily a CD-R). This would mean that this dye could be prepared much more cheaply and would therefore enable more cost-effective production.

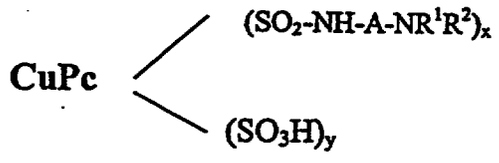
Therefore the invention provides a write-once optical data carrier containing a transparent plastics substrate to the surface of which is applied a writable information layer and optionally a reflection layer, characterised in that at least one phthalocyanine dye of the general formula I is present in the writable information layer.

The invention also provides a process for producing a moulded part consisting of a transparent substrate to the surface of which is applied a writable information layer

containing a dye, wherein the dye contains a phthalocyanine dye of the general formula I and is worked up using a solvent mixture.

The invention also provides use of the phthalocyanine dye of the formula I, in particular sulfonamide group-containing copper phthalocyanine dyes of the formula I, in optical data carriers.

The phthalocyanine dye according to the invention can be represented by the formula given below:



in which

CuPc represents a copper phthalocyanine group,

A represents an optionally substituted straight chain or branched C_2-C_6 alkylene such as e.g. ethylene, propylene, butylene, pentylene, hexylene,

R^1 and R^2, independently, represent hydrogen or each optionally represent a substituted straight chain or branched C_1-C_6 alkylene such as e.g. methylene, ethylene, propylene, butylene, pentylene, hexylene, in particular a substituted C_1-C_6 hydroxyalkyl group as well as an unsubstituted C_1-C_6 alkyl group, or R^1 and R^2, together with the nitrogen atom to which they are bonded, form a heterocyclic 5- or 6-membered ring which optionally contains another heteroatom, e.g. S, N or O,

x is 2.0 to 4.0,

y is 0 to 1.5 and

the sum of x and y is 2.0 to 4.0, preferably 2.5 to 4.0.

Mixtures of the dyes mentioned above may also be used.

Production of the write-once optical data carrier according to the invention is achieved by spin-coating the dye itself or the dye in combination with other dyes or with suitable solvents onto a transparent substrate. For coating purposes, the dye, with or without additives, is dissolved in a suitable solvent or solvent mixture in such a way that the dye constitutes 100 or fewer parts by weight to 100 parts by weight of solvent. Then this primary dye solution can be diluted with a further suitable solvent in such a way that the dye constitutes 20 or fewer parts by weight to 100 parts by weight of solvent. The writable information layer is then metallised under reduced pressure, by sputtering or vapour deposition, and then provided with a protective lacquer.

The substrates may be produced from optically transparent plastics which, if required, have been subjected to surface treatment. Preferred plastics are polycarbonates and polyacrylates, as well as polycycloolefins.

Solvents and solvent mixtures for use when applying a coating of the dye are chosen, on the one hand, for their ability to dissolve the dye and, on the other hand, for having a minimal effect on the substrate. Solvents which are good at dissolving dyes according to the invention are e.g. benzyl alcohol and water acidified with acetic acid. Suitable solvents which have a small effect on the substrate are alcohols, ethers, hydrocarbons, halogenated hydrocarbons, Cellosolve, ketones. Examples of such solvents are methanol, ethanol, propanol, 2,2,3,3-tetrafluoropropanol, diacetone alcohol, tetrachloroethane, dichloromethane, diethyl ether, dipropyl ether, dibutyl

ether, methylcellosolve, ethylcellosolve, 1-methyl-2-propanol, methylethyl ketone, 4-hydroxy-4-methyl-2-pentanone, hexane, cyclohexane, ethylcyclohexane, octane, benzene, toluene, xylene. Preferred solvents are hydrocarbons and alcohols because they exert the smallest effect on the substrate.

Particularly suitable solvent mixtures for dyes according to the invention are those consisting of benzyl alcohol or water acidified with acetic acid mixed with the solvents mentioned above. The initial preparation of a solution in benzyl alcohol or water acidified with acetic acid followed by dilution with one of the solvents mentioned above is particularly preferred.

Suitable additives for the writable information layer are stabilisers, wetting agents, binders, diluents and sensitisers.

The reflection layer may be prepared from any metal or metal alloy which is conventionally used for writable optical data carriers. Suitable metals or metal alloys may be vapour deposited and sputtered and contain e.g. gold, silver, copper and their alloys with each other or with other metals.

The protective lacquer on top of the reflection layer may consist of UV-curing acrylates.

An intermediate layer which protects the reflection layer from oxidation may also be present.

Writable optical data carriers according to the invention may contain pre-written Read Only Memory (ROM) areas, as described in US 4940618 (Taiyo Yuden). The surface of the substrate may contain a separate thermally deformable layer, as described in US 4990388 (Taiyo Yuden).

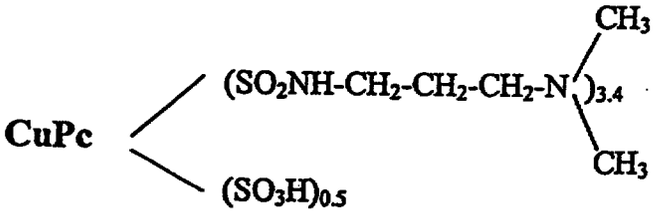
Examples

The following preparative examples illustrate the preparation of dyes according to the invention.

Example 1

138 g copper phthalocyanine are introduced into 700 g chlorosulfonic acid for 1 hour with stirring. The mixture is heated to 136°C - 138°C over 1 hour and held at 136°C - 138°C for 6 hours. The mixture is cooled to 85°C, 130 g of thionyl chloride are allowed to run in at 85°C - 90°C over the course of 2 hours and stirring is then continued for 4 hours at 90°C. After cooling to 20°C - 30°C, the reaction mixture is discharged onto a mixture of 1 l water and 1 kg ice. Furthermore, the temperature is maintained at 0°C by adding ice. The precipitated sulfochloride is filtered off under suction, washed with about 1 l of ice water and dried under suction. The moist filter cake (about 800 g) is introduced into a mixture of 250 ml water and 250 g ice and the pH is adjusted to 7 at 0°C using 10 % strength caustic soda solution. Then 129 g 1-amonium-3-dimethylaminopropane are allowed to run in, wherein the pH rises to about 10.5. The mixture is allowed to warm up to 20°C with stirring, the temperature is maintained at 20°C for 1 hour, heated to 40°C and then stirring is continued for 1 hour at 40°C. The pH is maintained at about 10 for the entire time using 10% strength caustic soda solution. The mixture is allowed to cool to room temperature, the pH is adjusted to 8.5 using dilute sulfuric acid, washed with 1 l water in portions and dried under vacuum at 60°C - 80°C.

269 g of dye which corresponds to the approximate formula II when in the form of the free acid are obtained.

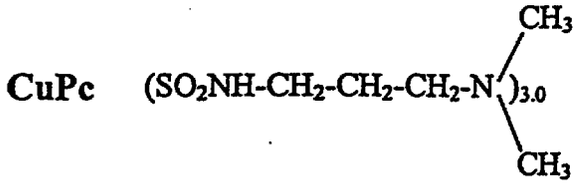


formula II

Example 2

138 g copper phthalocyanine are introduced into 460 g chlorosulfonic acid for one hour with stirring. The mixture is heated to 110°C - 112°C over 1 hour and held at 110°C - 112°C for 5 hours. The mixture is cooled to 85°C, 85 g of thionyl chloride are allowed to run in at 85°C - 90°C over the course of 2 hours and stirring is then continued for 3 hours at 90°C. After cooling to 20°C - 30°C, the reaction mixture is discharged onto a mixture of 1 l water and 1 kg ice. Furthermore, the temperature is maintained at 0°C by adding ice. The precipitated sulfochloride is filtered off under suction, washed with about 1 l of ice water and dried under suction. The moist filter cake (about 740 g) is introduced into a previously made up mixture of 840 ml ice water and 167 g of 1-amino-3-dimethyl-aminopropane over the course of 1 hour and with cooling. The temperature should then increase and at the end of the introduction procedure is raised first to 40°C and then to 70°C. The temperature is held at 70°C for 1 hour, the product is filtered under suction, washed with 1 l warm water in portions and dried under vacuum at 60°C - 80°C.

252 g of dye which corresponds to the approximate formula III when in the form of the free acid are obtained.



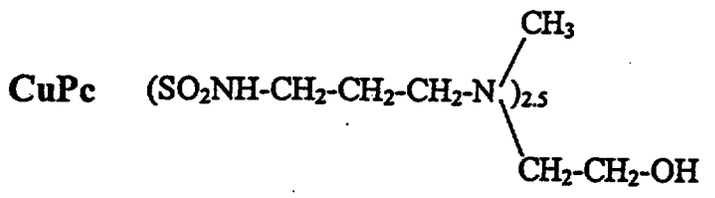
formula II

Example 3

138 g copper phthalocyanine are introduced into 500 g chlorosulfonic acid for one hour with stirring. The mixture is heated to 100°C - 102°C over 1 hour and held at

100°C - 102°C for 6 hours. The mixture is cooled to 80°C, 176 g of thionyl chloride are allowed to run in at 80°C over the course of 2 hours and stirring is then continued for 4 hours at 80°C. After cooling to 20°C - 30°C, the reaction mixture is discharged onto a mixture of 1 l water and 1 kg ice. Furthermore, the temperature is maintained at 0°C by adding ice. The precipitated sulfochloride is filtered off under suction, washed with about 1 l of ice water and dried under suction. The moist filter cake (about 740 g) is introduced into a previously made up mixture of 700 ml ice water and 150 N-methyl-N-(3-aminopropyl)-ethanolamine over the course of 1 hour with cooling. The temperature should then increase and at the end of the introduction procedure is raised first to 40°C and then to 70°C. The temperature is held at 70°C for 1 hour, the product is filtered under suction, washed with 1 l warm water in portions and dried under vacuum at 60°C - 80°C.

256 g of dye which corresponds to the approximate formula III when in the form of the free acid are obtained.



formula IV

The substituents guarantee a solubility of more than 50% in benzyl alcohol, and high solubility in water acidified with acetic acid.

The following examples explain the invention in more detail.

Example 4

A 7.5% solution of the dye in benzyl alcohol was prepared at room temperature. This solution was applied to a pregrooved polycarbonate substrate by means of spin-coating. The pregrooved polycarbonate was produced as a disk by means of injection moulding. The dimensions of the disk and the groove structure corresponded to those which are normally used for CD-Rs. 100 nm of Au was vapour deposited onto the disk with the dye layer as an information carrier. Then a UV-curing acrylic lacquer was applied by means of spin-coating and cured with a UV lamp. Using a commercial test writer for CD-Rs (Pulstec OMT 2000 x 4), it was not possible to enter any information because the pregrooved structure was so damaged, due to attack by the solvent benzyl alcohol, that the track sequence mechanism no longer functioned.

Example 6

A 37.5% solution of the dye in benzyl alcohol was prepared at room temperature. This stock solution was diluted with diacetone alcohol to give a 7.5% dye solution. This solution was applied to a pregrooved polycarbonate substrate by means of spin-coating. The pregrooved polycarbonate was produced as a disk by means of injection moulding. The dimensions of the disk and the groove structure corresponded to those which are normally used for CD-Rs. 100 nm of Au was vapour deposited onto the disk with the dye layer as an information carrier. Then a UV-curing acrylic lacquer was applied by means of spin-coating and cured with a UV lamp. Using a commercial test writer for CD-Rs (Pulstec OMT 2000 x 4), e.g. at 12 mW writing power and a 1x write speed (1.4 m/s), a modulation height of 47% (30 % to 70% is the CD-R specification) was obtained for the 3T signal and 69% (>60% is the CD-R specification) was obtained for the 11T signal when reading the information. The reflectivity in the grooves and on the flat sections was 72% and 75% respectively before writing. The specification for CD-Rs requires >70%. The molar absorption of

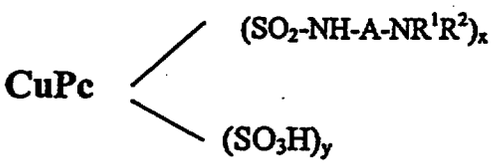
the dye, measured in benzyl alcohol, was about 40 000 l/(mol cm) with a λ_{max} at 690 nm and is thus much lower than the molar absorption of > 200 000 l/(mol cm) cited in US 5124067, which should be desirable for a dye for optical data storage.

Example 7

A 37.5% solution of the dye in benzyl alcohol was prepared at room temperature. This stock solution was diluted with diacetone alcohol to give a 7.5% dye solution. This solution was applied to a pregrooved polycarbonate substrate by means of spin-coating. The pregrooved polycarbonate was produced as a disk by means of injection moulding. The dimensions of the disk and the groove structure corresponded to those which are normally used for CD-Rs. 100 nm of Ag was vapour deposited onto the disk with the dye layer as an information carrier. Then a UV-curing acrylic lacquer was applied by means of spin-coating and cured with a UV lamp. Using a commercial test writer for CD-Rs (Pulstec OMT 2000 x 4), e.g. at 15 mW writing power and 2x write speed (2.8 m/s), a modulation height of 41% (30 % to 70% is the CD-R specification) was obtained for the 3T signal and 71% (>60% is the CD-R specification) was obtained for the 11T signal when reading the information. The reflectivity in the grooves and on the flat sections was 72% and 75% respectively before writing. The specification for CD-Rs requires >70%. The molar absorption of the dye, measured in benzyl alcohol, was about 40 000 l/(mol cm) with a λ_{max} at 690 nm and is thus much lower than the molar absorption of > 200 000 l/(mol cm) cited in US 5124067, which should be desirable for a dye for optical data storage.

Claims

1. An optical data carrier containing a transparent substrate to the surface of which is applied a writable information layer and optionally a reflection layer, characterised in that the writable information layer contains at least one phthalocyanine dye of the general formula I,



formula I



in which

CuPc represents a copper phthalocyanine group,

A represents an optionally substituted straight chain or branched C_2-C_6 alkylene,

R^1 and R^2, independently, represent hydrogen or each optionally represent a substituted straight chain or branched C_1-C_6 alkylene, in particular a substituted C_1-C_6 hydroxyalkyl group as well as an unsubstituted C_1-C_6 alkyl group,
or R^1 and R^2, together with the nitrogen atom to which they are bonded, form a heterocyclic 5- or 6-membered ring which optionally contains another heteroatom, e.g. S, N or O,

x is 2.0 to 4.0,

y is 0 to 1.5 and

* C L M S *

the sum of x and y is 2.0 to 4.0.

2. A process for producing a moulded part consisting of a transparent substrate to the surface of which is applied a writable information layer containing a dye, characterised in that the dye contains a phthalocyanine dye of the general formula I and is worked up using a solvent mixture.

3. A process according to Claim 2, characterised in that one component K1 in the solvent mixture is chosen from the group benzyl alcohol or water acidified with acetic acid, preferably benzyl alcohol.

4. A process according to Claim 3, characterised in that in a first step the dye is dissolved in component K1 and in a second step this solution is diluted with another component K2 which is chosen from the group formed by alcohols, ethers, hydrocarbons, halogenated hydrocarbons, Cellosolve, ketones, preferably chosen from the group formed by methanol, ethanol, propanol, 2,2,3,3-tetrafluoropropanol, diacetone alcohol, tetrachloroethane, dichloromethane, diethyl ether, dipropyl ether, dibutyl ether, methylcellosolve, ethylcellosolve, 1-methyl-2-propanol, methylethyl ketone, 4-hydroxy-4-methyl-2-pentanone, hexane, cyclohexane, ethylcyclohexane, octane, benzene, toluene, xylene.

5. A process according to one of Claims 2 to 4, characterised in that the information layer which contains the dye is applied by spin-coating.

6. Use of sulfonamide group-containing copper phthalocyanine dyes of the formula I for optical data storage.