An optical storage medium

The invention relates to a writable optical storage medium, particularly in the form of a singly- or multiply-writable compact disc (CD), which comprises a specific support layer.

Conventional writable optical storage media, particularly CD-Rs, in which data recording and read-out is effected with the aid of laser light, are built up from a transparent support, a recording layer comprising a metal such as Te, Bi or Mn or a dye such as a cyanine, merocyanine, phthalocyanine or azo dye, a metallic reflection layer, and optionally a protective layer also. Data recording is effected by irradiation with laser light through the transparent support. In the course of this procedure, the recording layer is deformed, sublimed, evaporated or modified at the irradiated points, so that pits are formed if necessary. A free space is also frequently formed between the recording layer and the adjacent layer. A reflecting metal layer of Au, Ag, Al or Cu is conventionally provided on the writable layer and a protective layer is provided in turn on the latter. Read-out is effected by irradiation with laser light of lower energy, likewise through the transparent support. The contrast between the light reflected from the pits and the light reflected from the remaining parts of the storage medium is read out as an electrical signal.

Conventional non-writable CDs (ROM type: read-only-memory) do not comprise the aforementioned writable layer, but simply comprise pits corresponding to the data to be reproduced, which are already formed on the support, e.g. by press moulding. Apart from this, their construction is relatively similar.

See A.B. Marchant, Optical Recording (1990), for a more precise explanation.

One problem with known CD-Rs is the relatively high sensitivity of the recording layer. The effect of the heat and of radiation can result in the recording layer being altered with the result that the CD-Rs are no longer writable and/or are no longer

readable. Thus some manufacturers recommend that CD-Rs are not exposed to direct sunlight. Equipment manufacturers advise that CD-Rs should not be played in DVD players, since it is feared that the shorter wavelength of the laser used in a DVD player could damage CD-Rs. The stored information can then only be read out subject to errors; this is measured with the aid of electronic test instruments and is quoted as, *inter alia*, the block error rate.

The block error rate gives, in summary form, the total number of defective information blocks and should be as low as possible. If the block error rate exceeds a value of 220, the data storage medium is outside the specification. The block error rate is determined using a CD test player. See W. Schild "Fehler vom Player, Fehler von der Platte", in Funkschau 23/1988, for more detailed information. It is also possible for CD-Rs to be altered to such an extent that they can no longer be read or written at all.

The object of the present invention is to provide writable optical storage media, particularly writable CDs, which exhibit improved stability and which thus have an improved service life.

The object is achieved according to the invention by the provision of a writable optical storage medium which comprises a protective layer, one or more writable layers, optionally a light-reflecting layer and at least one support layer, which is characterised in that the support layer contains at least one dye which has a transmission of at least 70% at the wavelength of the laser which is used for writing and/or reading and which has an absorption of at least 70% at all other wavelengths of visible light which are at least 100 nm shorter than the wavelength of the laser light.

The support layer preferably contains at least two dyes, particularly preferably three dyes, in order to achieve the desired absorption characteristics.

The dye or dyes are preferably selected from the group comprising anthraquinone and pyrazolone dyes. Makrolexgelb 3G® (a pyrazolone dye, Colour Index, Part 1: Solvent Yellow 93), Makrolexrot 5B® (an anthraquinone dye, Colour Index, Part 1, Solvent Red 52, Part 2 No. 68210) and Hytherm Blue E® (an anthraquinone dye, Colour Index Part 1 Solvent Blue 101) are particularly preferred.

The material for the support layer is not critical; there are no specific limitations. The support layer comprises conventional material used for optical storage media, particularly for CD-Rs, and in particular comprises a polymer which is transparent to the laser light used for writing and/or reading, such as poly(co)carbonates, polymethyl methacrylates, poly-4-methylpentene-1, amorphous cyclic polyolefines, polyesters, epoxy resins or polyacrylates. Poly(co)carbonate is used in particular. It may comprise information signals in the form of pits and/or control signals and/or guide channels, i.e. it may be a support with or without information signals which is optionally formatted. It may optionally be surface-treated in the conventional manner.

The dye or dyes are incorporated in the support material in the conventional manner, e.g. by compounding the dyes with or by depositing the dyes on granules of the support material. The dye may also preferably be added as a master batch.

The concentration of the dye or dyes in the support material is preferably 0.1 to 1.4 wt.%, particularly preferably 0.3 - 0.8 wt.%. The support is formed from the dye-containing material in the usual manner, e.g. by injection moulding or stamping.

If a plurality of support layers is provided, the layers preferably comprise the same polymer material. In this case, the dye or dyes can be incorporated in a single support layer or in a plurality of support layers.

The writable layer(s) which is/are optionally provided is/are preferably the conventional sensitive dye layer(s) (see EP-A 353 392, 488 231 and 410 879, for

example). These comprise one or more organic dyes such as phthalocyanines, merocyanines, cyanines, indodicarbocyanines, azulenes and azo dyes. They are deposited in the conventional manner, e.g. by spin-coating, for example as a solution in a solvent. Diacetone alcohol, fluorinated alcohols such as tetrafluoropropanol, butanol or mixtures thereof are used as solvents, for example.

The dyes of the writable layer(s) are different from the dyes of the support layer. Cyanine dyes are particularly preferred.

The reflecting layer which is optionally provided preferably comprises a metal with a reflection of more than 80% at the wavelength of the laser light which is used, such as Au, Ag, Al, Cu or an alloy thereof, for example. It can be applied, for example, by a deposition process from the gas phase, such as vacuum deposition, sputtering, ion-plating or similar techniques.

The protective layer comprises a resin with an outstanding resistance to impact, which is conventionally an epoxy resin, a polyacrylate resin, or a hardened silicone resin. The protective layer is conventionally formed by deposition of the resin by spin-coating, followed by UV irradiation for curing. However, it may also comprise a flexible material, such as a polyurethane resin, for example.

The layer thicknesses of the individual layers are preferably 0.5 - 1.2 mm (support), up to 200 nm (writable layer), up to 200 nm (reflecting layer) and 5 - 200 μm (protective layer).

The wavelength of the laser for writing and/or reading is preferably 760 - 800 nm, particularly preferably 775 - 785 nm; or 620 - 660 nm, particularly preferably 635 - 650 nm.

The following examples further explain the invention.

The relative viscosity of the polycarbonate is measured using a 0.5% solution of the polycarbonate in methylene chloride at 25°C.

Examples:

Example according to the invention:

The following mixture is prepared as a support material:

99.6224 wt.%	granular polycarbonate, Makrolon CD 2005 supplied by Bayer AG, a polycarbonate of bisphenol A comprising tert.-butylphenol terminal groups, with an average solution viscosity of 1.20 (as measured in methylene chloride at 25°C, at a concentration of 0.5 g in 100 ml methylene chloride),
0.06513 wt.%	pyrazolone dye Macrolexgelb 3G (listed in the Colour Index, Part 1, as Solvent Yellow 93), Bayer AG,
0.19746 wt.%	anthraquinone dye Macrolexrot 5B (listed in the Colour Index, Part 1, as Solvent Red 52), Bayer AG,
0.11501 wt.%	anthraquinone dye Hythermblue E (listed in the Colour Index as Solvent Blue 101).

The dyes are intensively mixed with the granular material in a closed vessel, and thereafter the mixture is compounded in a twin-screw Werner Pfleiderer kneader, Type ZSK 53, at a material temperature of about 240°C.

CD-R blanks, of thickness 1.2 mm and external diameter 120 mm, are then produced using a CD-R stamping tool in a CD injection moulding machine. CD-R production is effected at a material temperature of 330°C and a mould temperature of 100°C, with a cycle time of 10 seconds. The CD-R stamping tool has a pre-groove disposed in the form of a spiral with an average width of 75 nm, an average depth of 180 nm and a track spacing of 1.6 μm.

The transmission is measured on the CD-R blanks. Figure 1 shows that the material has a high absorption at wavelengths less than 700 nm (measurement geometry: 0°/diffuse).

Comparative example

For comparison, CD-R blanks are produced which are analogous except that no dyes are added to the Makrolon CD 2005 substrate material. Figure 2 shows that the material has a high transmission over the entire visible light spectrum (measurement geometry: 0°/diffuse).

A dye layer is subsequently deposited on the CD-R blanks. The cyanine dye OM57 supplied by Fuji is used as the dye, in combination with the Kayasorb IRG-022 quencher supplied by Nippon Kayaku Co. The dye to quencher ratio is 20:1. Dye/ quencher deposition was effected from a diacetone alcohol solution by means of spin-coating, the conditions being selected so that an average dye layer thickness of 150 nm is formed.

A gold layer of thickness 60 to 80 nm is subsequently evaporated on to the dye layer. This gold layer is in turn provided with a protective lacquer of thickness about 10 μm.

The CD-Rs which are obtained according to the invention and from the comparative test are subsequently written in a Yamaha CD-R 100 burner at a write/read ratio of 4. The block error rate (BLER) of the CD-Rs is subsequently measured using an ISEDD test player supplied by the Ingenieurbüro für Umwelttechnologie und Meβtechnik, Bielefeld, in which a Philips and a Sony player are integrated.

The quality of the CD-Rs is of a comparable level, as shown in Table 1 below:

Table 1

	BLER (Sony)	BLER (Philips)
CD-R according to the invention	60	59
CD-R without dye in the substrate material	62	64

The CD-Rs according to the invention and the comparison CD-Rs are subsequently subjected to an exposure test according to ISO 4892-2. Exposure is effected through the substrate material on to the CD-R dye layer, under the following test conditions:

apparatus:	Atlas Xenon-WOM
light source:	6.5 kW XENON lamp (Atlas)
intensity of irradiation:	0.35W m^2*nm), measured at 340 nm
filtering:	pyrex/pyrex
black standard temperature:	65°C
test room temperature:	42°C
rel. atmospheric humidity:	65%
spray cycle:	102/18 minutes

Thereafter, the block error rates are again measured using the ISEED test player.

The comparison CD-R exhibit a significant increase in BLER, even after an exposure time of about 10 hours. After an exposure time of about 20 hours, the value of the BLER was about 500, i.e. way outside the specification.

The CD-R according to the invention exhibit no increase in BLER up to practically 50 hours' exposure time.



Claims:

1. A writable optical storage medium comprising a protective layer, one or more writable layers , optionally a light-reflecting layer and at least one support layer, characterised in that the support layer contains at least one dye which has a transmission of at least 70% at the wavelength of the laser which is used for writing and/or reading and which has an absorption of at least 70% at all other wavelengths of visible light which are at least 100 nm shorter than the wavelength of the laser light.

2. An optical storage medium according to claim 1, characterised in that the support layer contains at least two dyes.

3. An optical storage medium according to one of claims 1 or 2, characterised in that the transmission is at least 80%, preferably 85%, and the absorption is at least 90%, preferably 95%.

4. An optical storage medium according to one of claims 1 to 3, characterised in that the wavelength of the laser for writing and/or for reading is 760 - 800 nm, preferably 775 - 785 nm.

5. An optical storage medium according to one of claims 1 to 3, characterised in that the wavelength of the laser for writing and/or for reading is 620 - 660 nm, preferably 635 - 650 nm.

6. An optical storage medium according to one of claims 1 to 5, characterised in that the dye or dyes are selected from the group comprising anthraquinone or pyrazolone dyes.

7. An optical storage medium according to one of claims 1 to 6, characterised in that the dye or dyes are selected from Makrolexgelb 3G®, Makrolexrot 5B® or Hytherm Blue E®.

8. An optical storage medium according to one of claims 1 to 7, characterised in that the support layer contains 0.1 - 1 wt.% dye.

9. An optical storage medium according to one of claims 1 to 8 in the form of a singly- or multiply-writable compact disc.

10. An optical storage medium according to claim 9, characterised in that the writable layer consists of a sensitive dye which is different from the dye or dyes.

