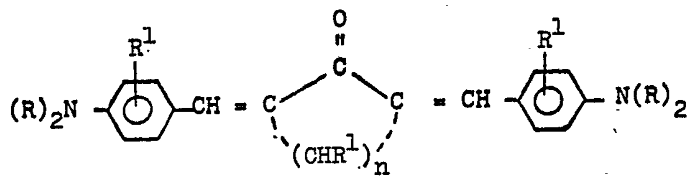
(12) UK Patent Application (19) GB (11) 2 070 977 A

(21) Application No **8105725**
(22) Date of filing **24 Feb 1981**
(30) Priority data
(31) **124382**
(32) **25 Feb 1980**
(33) **United States of America (US)**
(43) Application published **16 Sep 1981**
(51) **INT CL[3] G11B 7/24**
(52) Domestic classification **B2E** 1721 407U 415S 423T 489T M
(56) Documents cited **None**
(58) Field of search **B2E**
(71) Applicant
Eastman Kodak Company
343 State Street
Rochester
New York 14650
United States of America
(72) Inventors
Donald Paul Specht
Harold Todd Thomas
(74) Agents
L A Trangmar BSc
Kodak Limited
Patents and Trade Marks Department
PO Box 114
246 High Holborn
London WC1V 7EA

(54) **Optical recording materials containing *α,α'*-bis(dialkylaminobenzylidene) ketone dyes**

(57) Optical recording materials for recording information encoded in a high-energy density beam of radiaton at a wavelength of about 488 nm are disclosed.

The materials comprise a support having coated thereon a layer of an amorphous composition having an absorption factor of at least 20 litres per gram-centimetre at said wavelength, the layer comprising a binder and a dye which conforms to the structural formula:



wherein:

each R independently represents a substituted or unsubstituted straight- or branched-chain alky group having from 1 to 6 carbon atoms,

each R^1 independently is a hydrogen atom or a substituent which does not adversely affect the chromophore, and

n is 0 or an integer from 1 to 5, provided that when n is 0, either the two carbon atoms attached to the carbonyl group are joined by a single bond or each of the two carbon atoms bears a hydrogen atom.

SPECIFICATION

Optical recording materials containing α,α-bis(dialkylaminobenzylidene) ketone dyes

The present invention relates to the use of certain ketone dye compositions in optical recording materials. The ketone dyes have a high extinction coefficient at 488 nm, have good solubility in organic solvents and are compatible with common binders. Thus, the present invention relates to optical recording materials which have a layer comprising an amorphous material including a binder and the described dye.

Materials for recording information by thermally altering the physical structure of a material are known. One such material comprises a layer of a plastic material solvent coated on a support. The plastic material can be thermally deformed by a writing beam (usually a laser beam) so that some of the plastic material is displaced in the area illuminated by the beam. This deformation pattern retains its shape after the writing beam is "removed". The resulting deformation pattern can be read by projecting the pattern onto a viewing screen.

More recently, materials and means have been provided for rapidly recording large amounts of digital information in a small area. These materials provide a method of recording video information which can be read back with a high signal-to-noise ratio (SNR). These materials employ a thin recording layer of a certain metallic or organic material which is vacuum-deposited on a support. Recording is acomplished by a beam of high-energy density radiation, such as a laser beam. Typically, the laser beam is focused onto the surface of the recording layer of the material. Irradiated portions of the recording layer absorb energy from the laser beam so that small portions of the layer burn, evaporate or are otherwise displaced from these portions. This technique is usually referred to as "ablative recording". Normally, there is continuous motion between the laser and the layer so that, as the laser is pulsed or modulated, discrete pits or holes of varying sizes are created in the layer. The sizes and spacing of these holes constitute the encoded information. One material of this type is commonly referred to in the art as a "video disc".

Video discs of the ablative type can be read back using a laser beam similar to the one used to record the information. In conventional ablative video discs, the reading beam must also be significantly absorbed by the recording layer. A continuous reading beam is focused on the recording layer and the difference in optical density between pitted and unpitted areas is detected by a photodetector. It will be readily apparent that the recording layer must absorb significantly less energy from the reading beam than it absorbs from the writing beam if physical damage to the recording is to be avoided. This is usually accomplished by using a reading beam of much less power than the writing beam.

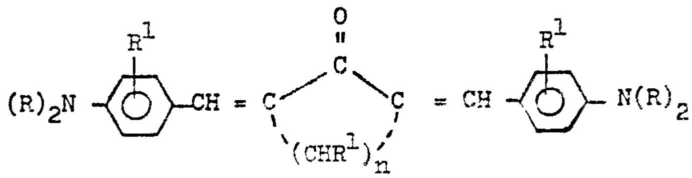
It has recently been discovered that, if the deformations which are formed in the recording layer are of a certain type, the information represented by these deformations can be read using a reading beam which is not absorbed by the recording layer. By using a layer of amorphous material having an extremely high absorbency, it has been found that deformations having sharply defined ridges can be formed. It is theorized that the ability to read with a laser which is not absorbed by the recording layer is the result of light scattering or phase shift from the sharply defined ridges. For whatever reason, it is now possible to use a higher-power laser read beam which in turn provides a comparatively high signal-to-noise ratio output. The recording material and method for reading are described in Patent Cooperation Treaty International Publication No. WO 79/00404 published 12 July 1979, based on International Application No. PCT/US 78/00227 (Thomas and Wrobel).

In the method of Thomas and Wrobel described in the preceding paragraph, it is desirable to provide a recording layer which is as high as possible. It was determined that an absorption factor in excess of 20 was necessary to produce the deformations which were readable by a read beam which was not absorbed by the recording layer. The absorption factor is defined as the product of the weight percent of dye included in the dye-binder compositions and the molar extinction coefficient of dye at the wavelength of the recording beam ($\varepsilon\lambda$), divided by the molecular weight of the dye (MW). The absorption factor is recited in terms of units of litres per gram-centimetre. Thus, the maximum absorption factor of a particular dye-binder amorphous recording composition is limited by both the extinction coefficient and the compatability of the dye with the binder. One high-energy density radiation source in an argon-laser which emits at about 488 nm. When recording using this laser, it is desirable that the dye which is in the amorphous composition have an extremely high extinction coefficient at this wavelength. Furthermore, it is desirable that the dye be compatible with the binder in high concentrations. While the materials disclosed in the Thomas and Wrobel application cited in the previous paragraph provide for absorption factors high enough to permit the necessary types of deformations to be formed, materials which provide still higher absorption factors have been sought.

Dyes have been discovered whose properties make them particularly useful in video disc recording materials. These dyes have extremely high extinction coefficients at 448 nm and have excellent solubility in common organic solvents. These dyes are compatible in high concentration with binders which are useful in video disc recording layers and can be used in these layers to provide extremely high absorption factors.

The dyes are (4-dialkylaminobenzylidene) ketones.

In accordance with the present invention, there is provided a material for recording information encoded in a high-energy density beam of radiation at a wavelength of 488 nm, the material comprising a support having coated thereon a layer of an amorphous composition having an absorption factor of at least 20 litres per gram-centimetre at said wavelength, the layer comprising a binder and a dye which conforms to the structural formula:



wherein:

each R independently represents a substituted or unsubstituted straight- or branched-chain alkyl group having from 1 to 6 carbon atoms,

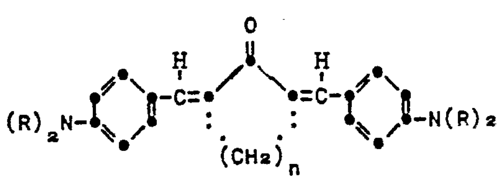
each R^1 independently is a hydrogen atom or a substituent which does not adversely affect the chromophore, and

n is 0 or an integer from 1 to 5, provided that when n is 0, either the two carbon atoms attached to the carbonyl group are joined by a single bond or each of the two carbon atoms bears a hydrogen atom.

In accordance with another aspect of the invention there is provided a method of recording information encoded in a high-energy density beam of radiation at a wavelength of 488 nm which method comprises focussing the beam on the recording layer of a recording material of the invention and scanning the beam relative to the recording layer to produce deformations in the layer which correspond to the encoded information.

An information record in a material of the present invention comprises a plurality of deformations in a layer of an amorphous dye-binder composition described above. Preferably, the deformations have a size smaller than 1.5 microns and comprise a depression surrounded by a sharply defined ridge. These deformations are such that they are detectable using a beam of high-energy density radiation which is not absorbed by the amorphous composition.

Useful dyes according to the present invention conform to the structure:



These dyes have extinction coefficients which are very high at 488 nm, typically having a molar extinction coefficient at this wavelength which exceeds 65,000. In addition, the dyes are compatible at relatively high concentrations with common binders which make them useful in video disc applications. The dyes are soluble in common solvents such as cyclohexanone, acetone, benzene and xylene.

Each R in the structural formula above is alkyl as described e.g. methyl, ethyl, isopropyl or *t*-butyl. For the purposes of the invention, dyes having substituted alkyl groups such as, for example, halogen-substituted alkyl, e.g., chloromethyl and bromoethyl, are considered to be equivalent. Further, the benzylidene group can be substituted with groups other than the alkylamino group in other positions so long as these substituents do not adversely affect the chromophore. The cyclic ketone ring, when present, can be similarly substituted. Useful substituents include, for example, halogen and lower alkyl. However, dyes not having these substituents are preferred because these substituents add to the molecular weight and therefore decrease the value of $\epsilon\lambda/MW$.

The dyes described above can be made by reacting acetone or a cyclic ketone such as cyclopentanone with a dialkylaminobenzaldehyde. The starting materials for making the dyes useful in the present invention are well-known in the art. The dyes are made by condensing the aldehyde and the ketone in an alkaline solution comprising an organic solvent. The solution can be made alkaline by the addition of suitable base such as potassium hydroxide or sodium hydroxide. Useful organic solvents include methanol and ethanol. The reaction solution may be heated under reflux to produce the desired product.

Both the acetone-derived compounds and the cyclopropanone-derived compounds are intended to be included when n = 0 in the formula for the dyes given above.

Illustrative dyes which have been made by this method include:

2,5-bis(4-diethylaminobenzylidene)cyclopentanone

2,6-bis(4-diethylaminobenzylidene)cyclohexanone

1,3-bis(4-diethylaminobenzylidene)acetone

Other useful dyes include:

2,3-bis(4-dimethylaminobenzylidene)cyclopropane

2,5-bis[4-(N-*t*-butyl-N-methylamino)benzylidene]-cyclopentanone.

The described dyes are compatible with binders which are useful in making laser recording materials. By "compatible" is meant that the dye can be mixed with the binder in sufficient concentration to provide the required absorption factor, i.e., greated than 20, without crystallizing after a layer of the dye and binder is coated and dried. Typically, the described dyes are compatible in dye-binder compositions comprising at least 50 percent dye by weight, although higher concentrations and therefore higher absorption factors are possible. Because of the high extinction coefficient of the present dyes at 488 nm and their excellent compatibility with common binders, these dyes can be included in the composition over a very wide range of concentration while maintaining the absorption factor in excess of 20. This facilitates the optimization of the material.

Useful binders include any film-forming material which is capable of being deformed upon exposure to high-energy density radiation such as a laser beam. Useful binders include cellulose acetate butyrate, polystyrenes, polysulphonamides, polycarbonates, cellulose nitrate, poly(ethyl methacrylate) and poly(vinyl butyral). Combinations of binders may also be used. Cellulose nitrate is the preferred binder.

A useful laser recording material comprises a support having coated thereon a layer of the dye included in the binder. Depending upon the desired mode of reading the material, the support may either be reflective or transparent. In the case of a reflective support, both sides of the support may be reflective and a recording layer may be provided on both sides. The support may be any of a wide variety of materials including glass, a self-supporting polymer film such as poly(ethylene terephthatate) or cellulose acetate, or metal. The support must have a relatively high melting point in order to avoid deformation of the support during recording. The support is desirably very smooth to minimize noise and dropouts. In certain preferred embodiments, the support is coated with a smoothing layer prior to the coating of the reflective surface and the described dye-binder composition.

The composition which is used as a smoothing layer is preferably a low-viscosity, polymerizable fluid which can be coated on the surface of the support. Following coating, polymerization of the fluid produces a microsmooth surface on the support. The support can be made reflective by vacuum metalization of the smooth surface. In preferred embodiments, the polymerizable fluid comprises photopolymerizable monomers. Preferably, the monomers or mixtures of monomers are a low-viscosity fluid in the absence of a solvent. Useful polymerizable fluid compositions are described in U.S. Patents 4,092,173 and 4,171,979.

The recording layer comprising the described dye and binder can be coated by many of a wide variety of methods. Most conveniently, the dye and binder are coated from a common solvent or, alternatively, from a mixture of miscible solvents. The dye-binder composition can be coated by spray coating, air knife coating, whirl coating or by any other suitable method. The thickness of the recording layer according to the present invention is not critical; however, best results are obtained when the thickness of the layer is from about 0.1 to about 10 microns.

The described recording compositions are capable of producing depressions or holes surrounded by sharply defined ridges. This type of deformation can be read back using a read beam which is not significantly absorbed by the recording layer. By "sharply defined ridge" is meant that the ridge and hole/depression have noticeable boundaries and that, as measured in the plane of the undeformed outer surface of the layer, the width of the ridge is less than or equal to the breadth of the hole depression. These dimensions can be measured from an electron micrograph.

The invention is further illustrated by way of example as follows:

Preparation 1: Preparation of 2,5-bis(4-diethylaminobenzylidene)cyclopentanone

About 110 g of *p*-diethylaminobenzaldehyde were dissolved in a solution of 80 g of potassium hydroxide in 1000 mL of methanol. About 26 g of cyclopentanone were added with stirring and the reaction mixture was heated under reflux on a steam bath for 3 hr. After chilling in the freezer, a solid precipitate was collected, washed with alcohol and recrystallized from a mixture of alcohol and acetonitrile. The title compound was confirmed by its NMR spectrum. This dye has an ε_{488}/MW of 188 litres per gram-centimetre at 100% concentration of dye.

Example 1: Video recording element

A 110-mm-diameter circular glass substrate was whirl-coated with a surface-smoothing composition by flooding the glass substrate with the smoothing composition at low rpm (about 80–100 rpm) and then leveling the coating by advancing the speed to about 500 rpm. The surface-smoothing composition comprised:

pentaerythritol tetraacrylate	20 g
a low-viscosity urethane-acrylate monomer (UV-curable Topcoate (trade mark) 874–C–2002, Fuller O'Brian Corp)	20 g
2-ethoxyethanol	60 g
a coumarin sensitizer composition	3 g
surfactant	3 drops

The coated and dried surface-smoothing composition was cured by irradiating with a 3000-watt pulsed xenon arc lamp at 45.7 cm (18 in) for 4 min.

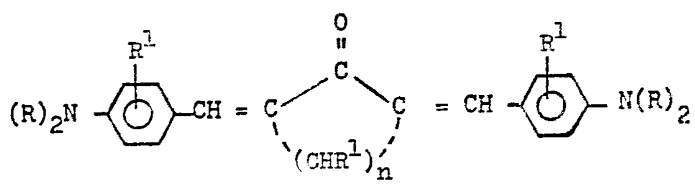
The thus smoothed surface of the substrate was then coated with a 500-Å-thick reflecting layer of aluminium by vapour deposition.

A recording layer was whirl-coated on the reflecting layer by flooding the reflecting layer with the dye-binder composition at low rpm and then leveling the coating at about 1300 rpm. the dye-binder composition was formed by dissolving 1 g of cellulose nitrate and 1 g of the dye prepared in Preparation 1 in 60 g of cyclohexanone. After drying, the absorption coefficient of the recording layer was 94 litres per gram-centimetre, and the disc was ready to use.

Tracks were recorded in the recording layer of the disc using an argon-ion laser-light beam (488 nm) focused with a numerical aperture NAg = 0.525 while the disc was rotating at 1800 rpm. (The term "NAg" represents the numerical aperture of the focused gaussian beam of light measured to its e^{-2} irradiance diameter.) The recorded tracks were then read back with a similarly focused helium-neon laser-light beam (633 nm) having a power of about 1 mW on the disc surface. For an incident write power of about 10 mW, the SNR on readout was about 50. In comparison, a recording layer which was the same as that of this example, except that the dye was 3,3'-carbonylbis(7-diethylaminocoumarin), required an incident write power of about 15 mW to produce a recording which could be read back with an SNR of 50.

CLAIMS

1. A material for recording information encoded in a high-energy density beam of radiation at a wave-length of 488 nm, the material comprising a support having coated thereon a layer of an amorphous composition having an absorption factor of at least 20 litres per gram-centimetre at said wavelength, the layer comprising a binder and a dye which conforms to the structural formula:



wherein:

each R independently represents a substituted or unsubstituted straight-or branched-chain alkyl group having from 1 to 6 carbon atoms,

each R^1 independently is a hydrogen atom or a substituent which does not adversely affect the chromophore, and

n is 0 or an integer from 1 to 5, provided that when n is 0, either the two carbon atoms attached to the carbonyl group are joined by a single bond or each of the two carbon atoms bears a hydrogen atom.

2. A material as claimed in Claim 1 wherein each R^1 represents a hydrogen atom.

3. A material as claimed in Claim 1 or Claim 2 wherein the support is reflective.

4. A material as claimed in any one of the preceding claims wherein the binder is cellulose nitrate.

5. A material as claimed in any one of the preceding claims wherein the dye is 2,5-bis(4-diethylaminobenzylidene)cyclopentanone, 2,6-bis(4-diethylaminobenzylidene)cyclohexanone or. 1,3-bis(4-diethylaminobenzylidene) acetone.

6. A material as claimed in Claim 1 substantially as hereinbefore described in Example 1.

7. A method of recording information encoded in a high energy density beam of radiation at a wave-length of 488 nm which method comprises focussing the beam on the recording layer of a material as claimed in any one of the preceding claims and scanning the beam relative to the recording layer to produce deformatons in the layer which correspond to the encoded

information.

8. A method as claimed in Claim 7 wherein the deformations have a size smaller than 1.5 microns and comprise a depression surrounded by a sharply defined ridge as hereinbefore defined.

9. A method of recording information as claimed in claim 7 substantially as hereinbefore described in Example 1.

10. An information record whenever produced by a method as claimed in any one of Claims 7 to 9.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd.—1981.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.