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(54) PROTECTIVE OVERCOAT LAYER FOR OPTICAL VIDEO DISC

(71) We, RCA CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of 30 Rockefeller Plaza, City and State of New York, 10020, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an optical recording medium. More particularly, this invention relates to an optical recording medium comprising a reflective layer coated with a light absorbing layer on a substrate and overcoated with a thin, hard, transparent layer.

Our Specification 1560245 describes an ablative recording system whereby a focussed modulated light beam, such as a laser beam, is directed at an ablative recording medium. The recording medium comprises a light reflecting material coated with a light absorbing material on a substrate. The thickness of the light absorbing layer is chosen to reduce the reflectivity to a minimum value so that maximum of light energy impinging on it is retained therein and is converted to thermal energy. This thermal energy causes the light absorbing material in the area struck by the light to ablate, thereby exposing selected portions of the light reflecting layer. During readout, the contrast between the light reflected from the absorbing layer, which is at the reflection minimum, and the light reflecting layer is detected.

Ongoing work in this area has resulted in the improved performance of the materials employed. Thus, in an illustrative embodiment of this recording medium, a substrate which is a flat, smooth non-conductor of heat is coated with a thin layer of a light reflecting material such as aluminum. The aluminum layer is passivated. The passivated aluminum layer is in turn coated with a layer of an organic light absorbing material such as 4 - phenylazo - 1 - naphthylamine.

Alternatively, as proposed in our Specification (52944/77) Serial No 1590296 the light reflecting layer is coated with a transparent dielectric material such as silicon dioxide. A thin layer of a metal is coated thereon to serve as the light absorbing layer. Titanium is the metal most frequently used for this light absorbing layer.

When an organic dye is used as the light absorbing layer, a continuing problem is the mechanical delicacy of the dye layer. A protective coating with good mechanical properties would make it easier to handle the recording medium without damage to the dye layer. In addition, an overcoat layer would protect the dye or metal light absorbing layer from reacting with the atmosphere, thereby extending the lifetime of the recording medium.

Another problem affecting both configurations of the recording medium is the effect of surface dust which precipitates onto the medium from the environment and causes signal defects or dropouts on readout or recording. As each dust particle moves under the focussed spot of the recording laser beam, it effectively shadows that portion of the track on which it lies, thus preventing the formation of information pits for the segment of the picture signal. On playback the section of recorded track which contained the dust particle exhibits a picture defect or dropout caused by the temporary loss of information. An improved recording medium would make it possible to remove dust safely without abrading or otherwise disturbing the light absorbing layer.

We have discovered an improved optical recording medium which comprises a light reflecting material coated with a light

absorbing material and overcoated with a thin layer of a solid, transparent, hard, inert material of a certain thickness. The protective overcoat permits wiping or washing of the recording medium to remove surface dust particles without disturbing the light absorbing layer. Additionally, it protects the light absorbing layer from chemical attack by the atmosphere.

According to the first aspect of the present invention there is provided a record blank for use with a recording laser beam providing light of a given frequency, said blank comprising:

a layer of light reflecting material which is reflective of light of said given frequency;

a layer of light absorbing material which is absorptive of light of said given frequency overlying said light reflecting layer; and

a solid, transparent, hard protective overcoat layer, such that surface contaminants can be removed from said overcoat, overlying said light absorbing layer, said protective overcoat comprising a material selected from the group consisting of derivatives of sucrose in which the hydroxyl groups of the sucrose are replaced by ester groups, pentaerythritol derivatives of rosin acids, and polymers formed from acetylene or perfluoromethylcyclohexane in a glow discharge.

A second aspect of the invention provides an information record for use in a playback apparatus using a playback light beam of a given frequency comprising:

a layer of light reflecting material which is reflective of light at said frequency;

a layer of light absorbing material which is absorptive of light at said frequency overlying said light reflecting layer, said absorbing layer having therein a succession of spaced pits representative of recorded information; and

a solid, transparent, hard, protective overcoat layer, such that surface contaminants can be removed from said overcoat, overlying said light absorbing layer;

wherein the material of said overcoat layer is selected from derivatives of sucrose in which the hydroxyl groups of the sucrose are replaced by ester groups, pentaerythritol derivatives of rosin acids, and polymers formed from acetylene or perfluoromethylcyclohexane in a glow discharge.

The light reflecting material can be coated on a substrate with an optically smooth, flat surface to which the subsequently applied light reflective layer is adherent. A glass or plastic plate or disc is suitable. The reflecting layer should reflect light at the wavelength employed for recording. A gold layer about 800 angstroms thick forms a good, non-reactive reflecting layer. An aluminum layer from about 250 to 500 angstroms thick is also sufficient for this purpose. The aluminum layer can be oxidized to a depth of about 30 angstroms in order to passivate the surface.

The light absorbing layer must be absorbing at the wavelength used for recording. In addition it should form an amorphous, coherent film of a thickness that minimizes light reflection. Further, the light absorbing layer should be readily ablatable at low temperatures to form clearly defined, regularly shaped holes. A layer of 4 - phenylazo - 1 - naphthylamine, obtained by evaporating the dye-stuff Sudan Black B in a vacuum chamber, forms an excellent coating. The light reflecting layer may be alternatively coated with a layer of silicon dioxide which, in turn, is coated with a thin layer of titanium.

Preferably, materials for the overcoats are hydrophobic and stable with respect to ambient conditions and any solution used to wash the recording medium. In addition, suitable materials usually should be amorphous and and nonscattering at the recording and readout wavelength. When the signal is recorded through the overcoat, the overcoat should allow formation of the signal elements beneath it and readout through it without substantially affecting picture quality. Therefore, the overcoat material should have a sufficiently high melting point and hardness to resist rupture during recording. Because the organic dyes used for the light absorbing layer are readily soluble in most organic solvents, a desired characteristic of an overcoat material is the capability of forming an amorphous layer by a non-solvent deposition process. Additionally, preferred materials will be able to withstand any mechanical stress introduced by routine handling.

The initial antireflection, light absorbing condition of the light absorbing layer can be preserved if the thickness of the thin protective overcoat layer is carefully controlled. Optimally, the thickness of an optically passive, non-reflecting overcoat layer will be equal to $m\lambda/2n$, where m is an integer, λ is the wavelength of the recording or readout light from the laser, and n is the refractive index of the overcoat material at the recording or readout wavelength.

Several organic materials have been identified as suitable for use as thin overcoats in the present invention. Derivatives of sucrose in which the hydroxyl groups on the sucrose are replaced by ester groups, such as acetyloxy or benzoyloxy groups, form good protective overcoats. In an illustrative embodiment a layer of sucrose benzoate, formed from sucrose in which six or more hydroxyl groups have

been replaced by benzoyloxy groups, is evaporated onto the light absorbing layer of the recording medium. Sucrose octa-acetate also can be applied by evaporation to form a good overcoat layer.

Another class of materials which form suitable overcoat layers for use in the present invention are pentaerythritol derivatives of the rosin acids. These materials are low molecular weight (3,000—7,000) thermoplastics which can be applied by evaporation. Pentaerythritol esters of partially or fully hydrogenated rosin acids, where the principle rosin acid component is abietic acid and the softening point is about 104°C., form good overcoats.

Highly crosslinked films prepared *in situ* by glow discharge or by polymerization of a reactive monomer deposited on the surface of the light absorbing layer are also good overcoat materials. Suitable films include those prepared by exposing to glow discharge either a mixture of acetylene and nitrogen (1:3 ratio), or perfluoromethylcyclohexane in an argon carrier gas.

The invention will be further explained by reference to the drawings, in which the three Figures show respectively a recording medium prior to and after recording, and a system for recording thereon and playback thereof.

Figure 1 shows a recording medium 24 of the invention prior to exposure to a recording light beam comprising a substrate 110, a light reflecting layer 112 with a transparent passivating layer 114 thereon, a light absorbing layer 116 and an overcoat layer 120 of sucrose benzoate.

Figure 2 shows a recording medium of the invention after exposure to a recording light beam wherein the light absorptive layer 116 has been ablated to leave a pit 118, exposing the passivating layer 114 to light while leaving the overcoat layer 120 intact. It will be understood that the recording medium after recording contains a plurality of pits 118 rather than the single one shown in Figure 2.

The use of the present recording medium can be explained in greater detail by referring to Figure 3. For recording, the light emitted by a laser 10 is fed to a modulator 12 which modulates the light in response to an input electrical signal source 14. The modulated light is enlarged by recording optics 16 to increase the diameter of the intensity modulated laser beam so that it will fill the desired aperture of an objective lens 18. The enlarged modulated laser beam is totally reflected by a polarizing beam splitter 20 and passes through a beam-rotating 1/4 wave plate 22 to the objective lens 18. The modulated recording beam then impinges upon a recording medium 24 as described in Figure 1 and ablates a portion of the light absorbing layer to expose a portion of the reflecting layer. The recording medium 24 is rotated by the turntable drive 26 at about 1800 rpm and may comprise a disc having a spiral track. A focus servo 28 maintains a constant distance between the objective lens 18 and the surface of the recording medium 24.

For readout, an unmodulated and less intense laser beam, that is, one that will not cause ablation in the recording medium, follows the same path as the recording beam to the recording medium 24. The recorded reflection-anti-reflection pattern modulates the reflected light back through the objective lens 18 and the 1/4 wave plate 22. The light, now rotated by 90° in polarization by each of the two passages through the 1/4 wave plate 22, (totalling 180° rotation), passes through the polarizing beam splitter 20 and is directed by playback optics 30 to a photodetector 32. The photodetector 32 converts the reflected light beam to an electrical output signal which is delivered to terminal 34 and which has amplitude variations corresponding to the input signal. A tracking servo 36 monitors the light through the playback optics 30 to ensure that the beam does not wander from the track during playback.

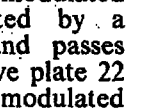
The present recording medium can produce high quality recordings with signal-to-noise ratios in the range of 45 to 50 decibels (dB), with average values of 48 dB. Light induced thermal recording on the organic dye layer through the overcoat layer is possible without reducing the signal-to-noise ratio more than about 5 dB. The above signal-to-noise ratio is within the range of broadcast standards. Recording media with lower signal-to-noise ratios are useful for consumer video disc or digitally encoded information records.

The invention will be further illustrated by the following example and comparative example, but the invention is not meant to be limited by the details described therein.

EXAMPLE 1

A disc 12 inches (30.5 centimeters) in diameter was coated with a gold layer 800 angstroms thick. A 4 - phenylazo - 1 - naphthylamine dye layer 400 angstroms thick was deposited on the gold layer, and an overcoat layer of sucrose benzoate was evaporated onto the dye layer.

The sucrose benzoate used had about 75 percent or more of the —OH groups on the sucrose replaced by



groups, where Ph is a phenyl moiety (C_6H_5—).

Before and after the application of the sucrose benzoate overcoat, recording was carried out by exposure to 50 nanosecond pulses of light having a wavelength of 4880 angstroms from an argon laser in an apparatus as in Figure 3. The sucrose benzoate layer was about 1630 angstroms in thickness.

The objective lens used for recording had a cover glass correction for about .08 millimeters. At a laser power setting of 250 milliwatts, the recording medium before overcoating with sucrose benzoate had a signal-to-noise ratio of 43 dB. After overcoating the recording medium had a signal-to-noise ratio of 40 dB. The sucrose benzoate overcoat remained intact.

Comparative Example

The following other overcoat materials were deposited on the organic dye layer as in Example 1. None of these materials formed an amorphous, optical quality film.

TABLE

Trade Name	Description	Comments
1) Piccotex LC (Hercules, Inc.)	A low molecular weight copolymer of vinyl toluene and α-methyl-styrene having a softening point of 90°C.	Hazy film
2) Piccotex 120 (Hercules, Inc.)	A low molecular weight copolymer of vinyl toluene and α-methyl-styrene having a softening point of 120°C.	Hazy film
3) Kristalex 3085 (Hercules, Inc.)	A transparent low molecular weight thermo-plastic derived from α-methyl-styrene with a softening point of 85°C	Poly-crystalline film
4) Kristalex 3100 (Hercules, Inc.)	A low molecular weight trans-parent resin derived from styrene derivatives and having a softening point of 100°C.	Poly-crystalline film
5) Stay-belite Ester 10 (Hercules, Inc.)	A glycerol ester of hydro-genated rosin with a soften-ing point of 83°C.	Poly-crystalline film

Attention is drawn to our associated inventions to which our copending Applications 16729/78 (Serial No 1603762) and 16730/78 (Serial No 1603763) are directed.

WHAT WE CLAIM IS:—

1. A record blank for use with a recording laser beam providing light of a given frequency, said blank comprising:

Before and after the application of the sucrose benzoate overcoat, recording was carried out by exposure to 50 nanosecond pulses of light having a wavelength of 4880 angstroms from an argon laser in an apparatus as in Figure 3. The sucrose benzoate layer was about 1630 angstroms in thickness.

The objective lens used for recording had a cover glass correction for about .08 millimeters. At a laser power setting of 250 milliwatts, the recording medium before overcoating with sucrose benzoate had a signal-to-noise ratio of 43 dB. After overcoating the recording medium had a signal-to-noise ratio of 40 dB. The sucrose benzoate overcoat remained intact.

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3) Kristalex 3085 (Hercules, Inc.)	A transparent low molecular weight thermo-plastic derived from α-methyl-styrene with a softening point of 85°C	Poly-crystalline film
4) Kristalex 3100 (Hercules, Inc.)	A low molecular weight trans-parent resin derived from styrene derivatives and having a softening point of 100°C.	Poly-crystalline film
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a layer of light reflecting material which is reflective of light of said given frequency;

a layer of light absorbing material which is absorptive of light of said given frequency overlying said light reflecting layer; and

a solid, transparent, hard, protective overcoat layer, such that surface contaminants can be removed from said overcoat, overlying said light absorbing layer, said protective overcoat comprising a material selected from the group consisting of derivatives of sucrose in which the hydroxyl groups of the sucrose are replaced by ester groups, pentaerythritol derivatives of rosin acids, and polymers formed from acetylene or perfluoromethylcyclohexane in a glow discharge.

2. A blank according to claim 1 wherein a layer of transparent dielectric material is situate between the light reflecting layer and the light absorbing layer.

3. An information record for use in a playback apparatus using a playback light beam of a given frequency comprising:

a layer of light reflecting material which is reflective of light at said frequency;

a layer of light absorbing material which is absorptive of light at said frequency overlying said light reflecting layer, said absorbing layer having therein a succession of spaced pits representative of recorded information; and

a solid, transparent, hard, protective overcoat layer, such that surface contaminants can be removed from said overcoat, overlying said light absorbing layer;

wherein the material of said overcoat layer is selected from derivatives of sucrose in which the hydroxyl groups of the sucrose are replaced by ester groups, pentaerythritol derivatives of rosin acids, and polymers formed from acetylene or perfluoromethylcyclohexane in a glow discharge.

4. An information record according to claim 3 wherein said light reflecting layer is passivated aluminium, and said light absorbing layer is 4 - phenylazo - 1 - naphthylamine.

5. An information record according to claim 4 wherein a layer of transparent dielectric material is situate between said light reflecting layer and said light absorbing layer.

6. An information record according to claim 5 wherein said light reflecting layer is aluminium, said light absorbing layer is titanium, and said dielectric layer is silicon dioxide.

7. A record blank or information record substantially as Example 1 hereinbefore described with reference to the drawings.

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