PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{4} **:** **G03C 1/72, 1/76, 5/16** **G01D 15/14, 15/34**	**A1**	**(11) International Publication Number:** **WO 88/ 03666** **(43) International Publication Date:** 19 May 1988 (19.05.88)

(21) International Application Number: PCT/US86/02404

(22) International Filing Date: 7 November 1986 (07.11.86)

(71) Applicant: OPTICAL RECORDING CORPORATION [CA/CA]; 141 John Street, Toronto, Ontario M5V 2E4 (CA).

(71)(72) Applicants and Inventors: WEST, John, L. [US/US]; 734 Emerson Avenue, Salt Lake City, UT 84105 (US). RUSSELL, James, T. [US/US]; 20626 11th Drive, S.E., Bothell, WA 98011 (US).

(74) Agents: COHN, Ronald, D. et al.; Fleit, Jacobson, Cohn & Price, 1217 E Street, N.W., Washington, DC 20004-1998 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), SU.

Published
With international search report.
With amended claims and statement.

(54) Title: RECORDING MEDIA INCORPORATING EXPLOSIVE COMPOUNDS

(57) Abstract

A recording medium utilizing explosive materials of explosion temperatures from about 100°C-350°C, such as metal azides as an energy amplifying substance. A photosensitive material comprises an energy absorptive dye and such an explosive material dispersed in an inert binder. Laser light absorbed by the dye is converted to thermal energy, causing the azide to decompose explosively, thus creating a void in the photosensitive material which can be read by an optical readout device.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BG	Bulgaria
BJ	Benin
BR	Brazil
CF	Central African Republic
CG	Congo
CH	Switzerland
CM	Cameroon
DE	Germany, Federal Republic of
DK	Denmark
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
HU	Hungary
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
RO	Romania
SD	Sudan
SE	Sweden
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
US	United States of America

RECORDING MEDIA INCORPORATING EXPLOSIVE COMPOUNDS

BACKGROUND OF THE INVENTION

The present invention relates to the recording of binary information on recording media. More particularly, the invention relates to recording media containing energy amplifying substances.

In recent years, data storage systems have been developed to store data permanently on a recording material by a beam of radiant energy. Recording with beams of high-intensity light, such as with an intensity modulated laser beam, is advantageous due to the small size of the spots which can be created.

While laser recording equipment for data storage systems has been developed to an advanced state, a precise and convenient recording media has not previously been found. Conventional photographic plates have been used but are disadvantageous because they require special handling and must be chemically processed before the data can be retrieved.

Some recording media, including those that contain chemical dyes which change color in response to heat or light and those that are thin films or tapes which are perforated by pulses of intense laser light, do not require chemical development. However, to record on such media it has been necessary to use high-intensity lasers in order to generate enough energy to make recording marks. The production of high-intensity laser light is much more expensive than the production of lower intensity laser light. It is, therefore, desirable to provide a recording medium which will record information when subjected to comparatively low intensity laser light.

BRIEF REFERENCE TO THE PRIOR ART

One approach to low intensity laser recording is disclosed in U.S. Patent No. 3,787,210, dated January 22, 1974, of Roberts. This patent describes a medium which employs a transparent substrate coated with heat-absorbing particles dispersed in a self-oxidizing binder. Specifically, Roberts refers to a recording film that comprises a substrate of an organic material coated with a material having heat-absorbing characteristics, such as carbon black particles, dispersed in a self-oxidizing binder such as nitrocellulose. As laser light strikes the medium, it is absorbed by the carbon black particles, and heat builds up to the point where combustion of the nitrocellulose is initiated. The combustion propels an area of the coating away from the substrate, leaving a clear spot surrounded by a dark background.

Because carbon black particles are used, the Roberts medium has a grain structure. This limits the resolution of the medium. Also, Roberts' use of a self-oxidizing binder further limits resolution and presents other problems. Nitrocellulose is a poorly defined substance formed by treating cellulose with mixtures of nitric and sulfuric acid. Widely different nitrocellulose products are obtained by varying the source of cellulose, strengths of acids, temperature, time of reaction, and the acid cellulose ratio. Exact reproduction of a particular nitrocellulose has proven to be difficult due to the numerous variables in the reaction process. Thus, a medium of the type described by Roberts would be difficult to manufacture in commercial quantities due to uniformity and other quality control problems. This is undesirable as it is important that the media obtained from different batches possess a constant sensitivity to laser light in order to ensure that the spots generated are of uniform size and can be spaced closely to achieve maximum data density.

Another approach to low intensity laser recording is described in U.S. Application Serial No. 143,827, filed April 25, 1980, of Moore et al. and its foreign counterparts, such as U.K. Patent No. 1,592,390. The described recording medium is a polymer material containing particles of reactant substance. In one example, reactant particles are made by combining a metal reducing agent with an oxidizing agent such as barium chromate to form a thermite type mixture. The reactant particles react exothermally upon exposure to laser light of sufficient intensity. This reaction chars the polymer material, thus creating dark areas which can be read by an optical digital scanner. Thus, in the recording method of Moore et al., a polymer binder is charred. Also, the reactant particles utilized in Moore et al. will produce a grain structure similar to that of the Roberts media, thus limiting resolution.

Rubner, U.S. Patent 4,287,294, discussed in context in more detail below, describes a photographic medium in which organic azides are used as photo-initiators.

de Bont et al., U.S. Patent 4,230,939, describes an information-recording element having a dye-containing auxiliary layer. It provides a transparent substrate, an auxiliary layer provided on the substrate, and a laser-reflective information recording layer provided on the auxiliary layer. This auxiliary layer or activating layer includes a laser light-absorbing dye. In the process of using the elements of the de Bont et al. patent, laser light is incident on and passes through the transparent substrate, traverses and is partly absorbed by the auxiliary layer, is then reflected against and partially absorbed by the information recording layer, again traverses and is partly absorbed by the auxiliary layer and ultimately leaves the element on the side of the substrate. The resultant temperature increases in the laser incident areas of the auxiliary layer and the information recording layer cause melting and hole formation in the information recording layer and in the auxiliary layer. The auxiliary layer may also include an endothermal material (i.e. a material capable of conversion via exothermal decomposition into thermal energy and pressure build-up) namely a polymeric endothermal material such as nitrocellulose or nitroglycerine-nitrocellulose mixtures which are used as explosive binders for the dye in the auxiliary layer. Picrates, for example the picric acid salt of the dye used in the auxiliary layer, are also suggested. However, none is specifically exemplified.

BRIEF SUMMARY OF THE INVENTION

It has now been discovered that these and other problems of the prior art may be significantly reduced or even eliminated by providing a recording medium matrix with a photosensitive material that includes a selected explosive material and a compatible, appropriately light absorptive dye. The explosive material may be chosen from metal azide explosive materials which exhibit suitably rapid exothermic decomposition at conditions achievable in localized areas under laser radiation of a wavelength and intensity commonly encountered in optical recording equipment, to cause ablation of the photosensitive layer and hence leave optically detectable indicia.

One particularly preferred example of explosive materials for use in the present invention is transition metal azides, especially those having explosion temperatures above about 100°C but below about 350°C, and which are capable of releasing significant amounts of energy on explosive decomposition. Thus the photosensitive material suitably includes a molecular dispersion of a metal azide. Such a matrix proves to be a very precise recording medium. When a pulse of moderate intensity light, e.g. laser light, strikes such a medium, that volume of the photosensitive material which is in the path of the pulse absorbs the light energy and is heated. This causes the molecules of the reactant substance, i.e. metal azide, in the heated volume predictably to react exothermally. The additional heat energy and gases liberated during the reaction are sufficient to create a void or hole in the photosensitive material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A particularly advantageous medium according to the present invention includes a substrate material which is coated with a photosensitive material, and a protective transparent covering which overlies the photosensitive material. The photosensitive material is a solid solution which includes a metal azide compound, a dye, and a binder. When a beam of light is directed at such a medium, light energy is absorbed by the dye which in turn transfers thermal energy to the azide. The azide explosively reacts liberating heat and nitrogen and creates a void or a hole in the photosensitive material. The void has different optical characteristics than the surrounding material which contains the dye and thus can be read by an optical scanner.

The photosensitive material of the invention does not utilize "grains" but rather includes homogeneously dispersed molecules of the metal azide and the absorbing dye. Because there are no "grains", the medium has very high resolution.

Some patents describe photographic media which form an image by the decomposition of organic azides. The images are formed by mechanisms that do not utilize heat released during decomposition. The organic azides are used as cross-linking agents, dye couplers, or initiators for polymerization. For example, in U.S. Patent No. 4,287,294 of Rubner, organic azides are used as photo-initiators. The organic azide in the Rubner patent absorbs the radiant energy and transfers this energy to an olefinically unsaturated polymer which initiates further polymerization or cross-linking. This is distinct from the present invention in which a void is created by heat and gas given off as a metal azide decomposes exothermally. The photosensitive material in the present invention is ablated, in contrast with the charring of the polymeric binder which occurs in the method of Moore et al. (U.K. Patent 1,592,390, op. cit.).

One object of this invention is to provide a digital recording medium which is able to utilize comparatively low intensity laser light as a recording source.

Another object of the invention is to provide a digital recording medium which, after being recorded upon, will provide high resolution when read by an optical scanner.

Another object of this invention is to provide a digital recording medium which, after being recorded upon, will provide a high signal to noise ratio when read by an optical read-out device.

These and other objects, advantages, and features of this invention will be apparent from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing:

FIG. 1 is a block diagram of an analog to digital optical recording system capable of producing a permanent record on the recording medium of the present invention; and

FIG.s 2 and 3 are side, cross section views of recording media according to the present invention.

DETAILED DESCRIPTION

Referring to FIG. 1, a typical device is shown for recording a binary data pattern by means of a radiant energy source, particularly a pulsed light source. The system includes a recorder unit 10 having its input connected to an audio-visual analog signal source 12, such as a microphone or television camera. This analog input signal 23 is applied to the input of an analog-to-digital signal converter 24 provided in the recorder unit 10 and which produces a digitally encoded electrical output signal 26. The output of the analog-to-digital signal converter 24 may be directly connected to an electrical optical digital signal recorder 28 through an amplifier 29 if it is desired to record the digital signal in real time simultaneously as it is generated. However, it may be desirable temporarily to store the digital signal 26 on the magnetic tape or other memory device of a digital computer 30 and to record such signals later at a more convenient time.

The electrical to optical digital signal recorder 28 converts the digital electrical signal into a digital light signal and records such light signal by scanning a pulsed light beam 40 of small spot size on a photosensitive recording medium to produce a track of digitally encoded spots which can be less than one micron in diameter. The spots are transparent in an opaque background, thus providing the ones and zeros of a binary code. The recording medium is supported, in a fashion which may be conventional, for movement in a path perpendicular to the optical axis and is mechanically coupled to a recording medium positioning mechanism 44 adapted for moving the medium to produce the track of digitally encoded spots. The recording medium positioning mechanism 44 may include a drive motor (not shown) which is energized selectively in response to signals transmitted by the optical digital signal recorder 28.

The recording medium 42 of the present invention includes a matrix interspersed with one or more explosives such as metal azides which are stable when exposed to light of first level of intensity, but which react exothermally when exposed to light at a second, higher level of intensity.

In FIG. 2, such a recording medium is shown as an active or recording layer 50 of photosensitive material, normally including a metal azide compound, a dye and a binder, on a smooth surface of a substantially transparent substrate 54. As described below, the active layer 50 can be a composite of two or more layers with the metal azide and dye in separate layers of the composite. A protective layer 56 may, optionally, be provided over the active layer 50 so that the protective layer 56 and substrate 54 protect opposite sides of the active layer from dust and other physical contaminants. Optionally, a thin reflective coating could be included on a surface 58 of the active layer 50 to reflect incident radiation 40a back into the active layer.

FIG. 3 shows a closely related embodiment for use with a beam 40b of incident radiation directed toward an active layer 60 rather than a substrate layer 64. In this embodiment, any protective layer 66 would be substantially transparent. And, if a reflective layer were used, it would best be located between the active layer 60 and the substrate 64.

In either embodiment, one or more subbing layers can be provided between the substrate and the active layer or between the protective layer and the active layer for the purposes described below. Such subbing layers must be substantially transparent if they are located in the path of the incident beam.

PHOTOSENSITIVE MATERIAL

A recording medium according to the present invention comprises a photosensitive material which includes an explosive material, particularly a metal azide. The metal azide reacts exothermally, when initiated, to amplify the energy of an incident radiation beam. Specifically, at the location where the beam strikes the photosensitive material, the exothermal reaction of the metal azide causes a heat build up and the formation of a visible mark or spot in the medium. The explosive material is preferably a primary explosive, i.e. one which gives a high velocity of escaping gases on decomposition.

Transition metal azides especially cupric azide constitute the most preferred class of explosive compounds for use in the present invention. Cupric, lead, and silver azides are well suited since they react highly exothermally and yet can easily be incorporated in a recording medium.

The medium may be formed by depositing a layer containing the metal azide on a substrate material. The metal azide can be applied to the substrate in a binder of polymeric material such as gelatin, e.g. from a solution thereof followed by spin drying. Alternatively, the metal azide may be applied directly by vapor deposition.

A typical medium according to the invention will have an active layer of photosensitive material that is 0.05-2.0, preferably 0.05-0.15 microns thick.

A further group of metal azides of possible use in the present invention, although not among the preferred explosive materials for use herein, comprises azides such as the azides of lithium, calcium, barium, zinc, and cadmium, mercurous azide, mercuric azide, trichlorotitanium azide and strontium, nickelous and manganous azides. All of these have explosion temperatures within the acceptable 100-350°C range. However, all of them are shock sensitive, and need handling with extreme care, and some of them present solubility problems, in that they are not significantly soluble in common organic solvents.

A further class of explosive materials suitable for use in the present invention is diazonium salts having a suitable degree of stability at room termperatures, but having explosion temperatures within the range 100-350°C. Specific examples of suitable diazonium salts are benzene diazonium nitrate and benzene diazonium perchlorate.

In general, any explosive material having suitable stability at room temperature, but having explosive decomposition temperatures in the range 100-350°C is suitable for use in the present invention.

A further class of explosives for use in the present invention is constituted by picric acid and its salts and picramic acid and its salts, which have explosive decomposition temperatures in the range 100-350°C. These compounds are, however, difficult and dangerous to handle, particularly if kept dry, so that they present storage, compounding and application problems in practice, and on these accounts are less preferred in the present invention.

In general, to be suitable for use in the present invention, an explosive material should be a primary explosive as opposed to a secondary explosive, and should have an explosion temperature in the approximate range 100°C-350°C, and preferably 150°C-250°C. It should have a reasonable degree of solubility in at least one organic or inorganic solvent, preferably an oxygenated organic solvent. It should be capable of generating significant amounts of heat on decomposition. In practice, the energy supplied by the incident laser radiation on making the optical record should be at least doubled by the thermal decomposition or explosion of the explosive material, and preferably is increased by at least 10 fold. It is further preferred that the granularity of the explosive material, and all other materials, in the photosensitive layer should be small, preferably less than 0.1 microns, to provide images of high optical resolution.

Advantageously, the photosensitive layer will also include a dye to facilitate absorption of energy from the energy source and conversion of the radiant energy into thermal energy. The dye should be selected for its ability to absorb radiant energy. In the case of a medium to be written by a laser beam, the dye should be selected to absorb light at the wavelength of the irradiating light. The dye efficiently absorbs the incident radiation of the laser, and converts the radiant energy to thermal energy to trigger the decomposition of the explosive material.

The recording media, in accordance with the present invention, can be used in conjunction with light radiation in the infrared, visible or ultraviolet regions, emanating from suitable laser sources emitting in those regions. It is only necessary to choose a dye which has absorption characteristics matching those of the chosen laser radiation. Suitable such dyes are known for use with laser radiation in the ultraviolet (250-350 nm) range, the visible (350-750 nm range) and the infrared (750-1150 nm) range.

A large number of dyes are suitable for use in conjunction with the metal azide recording medium. Those dyes which efficiently absorb the irradiating light and are soluble in suitable solvents are ideal. It is preferable to choose an explosive material, a binder and a dye which are significantly soluble in mutually compatible organic solvents. Then, the binder containing the explosive material can be deposited from a solution in a first solvent. Subsequently, the dye can be applied from solution thereof in a second, mutually compatible, but different solvent, so that it will diffuse into the explosive containing layer, but will not at the same time wash away that layer.

Useful dyes will be readily determinable by those skilled in the art, bearing in mind the wavelength of the selected laser for recording purposes. Identification of available dyes by their chemical class and structure, along with their radiation absorption characteristics, can be made from the available scientific literature.

For use in sensitizing a medium to the 514 nm output of an argon ion laser, the dyes erythrosin, erythrosin B, sudan III, rhodamine 6G and rose bengal are examples of suitable dyes.

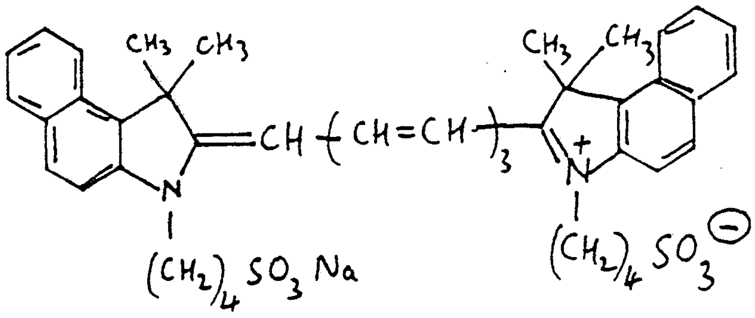
For use in sensitizing a medium to the output of common, low intensity, infrared laser radiation sources (750-1100 nm), useful dyes for the present invention will be found among the infrared dyes of the polymethine class and the squarylium class.

Since the chemical structures are often complicated, the dyes are commonly known by trivial names. From the guidelines and examples given herein, the available scientific literature and skill in the art, the operator should have no difficulty in selecting and using suitable dyes for the present invention in association with selected lasers and primary explosive.

Of the polymethine dyes, dicarbocyanines and tricarbocyanines are particularly preferred.

The following are specific examples of suitable infrared dyes for use in the present invention, in connection with common low-intensity laser radiation sources (750-1100 nm):

IR 125, of formula



HDITC;

IR 140;

IR 132;

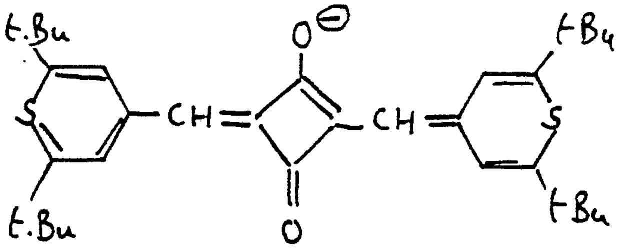
IR 144;

HITC (iodide or perchlorate);

DTTC;

Kodak dye 26;

Squarylium dyes, for example:



(Gravensteijn et al., Proceedings of S.P.I.E. 1983, 420, 327)

The photosensitive material may be formed to include the dye in at least two ways. The metal azide and dye can be applied as separate, but adjacent layers or can be intimately mixed in a single layer.

In a two layer system, for example, one can first form a layer consisting of a metal azide dispersed in a gelatin binder. A dye can then be applied as a coating using a 2% solution in methanol. For example, a solution of rose bengal can be poured on a metal azide layer, which is then spun at 1900 RPM until dry. The resulting photosensitive material is a homogeneous red layer with an absorption coefficient of about 1.5 at 514 nm.

IR 125 dye has been used to form plates sensitive at 830 nm. As with the red dyes above, for example the IR 125 dye is made into a 2% solution in methanol and coated on a metal azide/binder layer. The coated material is spun at 1900 RPM until dry, and a clear green photosensitive material results. Such material has a broad absorption band covering the 750-850 nm region of the spectrum. Thus, such photosensitive material can be used to manufacture media which are sensitive to the output of semiconductor lasers operating in this wavelength region.

Single layer photosensitive materials are desirable because the metal azide and dye are in intimate contact for maximum heat transfer to the metal azide and also because the material can be formed in a single coating step. It can sometimes be difficult to maintain both an explosive metal azide and a dye in a solution or suspension suitable for forming a layer. This can, however, be accomplished by use of solutions of metal azide precursors. Alternatively, a single layer can be formed by vacuum deposition.

Thus, to form a photosensitive material with a dye and an explosive metal azide in intimate contact, in a single layer, a dye can be applied in a solution which also contains a highly soluble, but nonexplosive, inorganic azide compound acting as a precursor for an explosive metal azide compound. Most suitable would be an alkali azide, such as sodium azide, which can be maintained in solution with a dye and which will react with an appropriate metal compound to provide one of the explosive metal azides mentioned above. For example, 2 grams of a dye and 2 grams of sodium azide can be dissolved in 100 ml of methanol. Plates of a suitable substrate material are coated with an appropriate metal salt in a gelatin binder. Then, the plates are immersed in the solution whereupon the sodium azide reacts with the metal salt to form an explosive metal azide. The plates are not washed with water but are just spun dry. The result is a plate coated with a single layer that includes both the explosive metal azide and the dye.

While the use of a dye is the most convenient way to utilize laser radiant energy to initiate an exothermic reaction in the metal azide, there are other possibilities. A medium would operate without a dye if the incident radiant energy was of a wavelength absorbed by the metal azide or by an adjacent binder material or subbing layer.

Substrates

Virtually any nonporous material with a smooth surface can be used as a substrate to support the photosensitive material. Glass plates of 0.060", 0.090" and 0.250" thickness have been used as have polymethylmethacrylate (PMMA), polyester, polyacetate sheets and polycarbonate sheets or films.

Substantially transparent materials would be required if it is desired to record by directing the incident beam through the substrate, as in the embodiment of Fig. 2.

In the embodiment of Fig. 3, polished metal plates or any reflective or clear plastic could be used as a substrate. Glass or a polymeric material, such as those listed above, can be plated with a material, such as gold or aluminum, to provide a substrate with a reflective surface on which to adhere the photosensitive layer.

Subbing Layers

Although a metal azide layer can be formed directly on any smooth surface, in many instances it is advantageous to provide a subbing layer between the photosensitive layer and the substrate. The subbing layer can improve the bonding of the photosensitive layer to some substrates and may have one or more additional uses.

It is difficult to form a smooth uniform layer of photosensitive material on some polymer substrates. Apparently the nature of the surface of some plastics affects the way films form. A subbing layer may serve to reduce the surface tension of the solution, resulting in a thin homogeneous coating. A subbing layer can also provide a smooth and receptive surface on which to apply the photosensitive material.

Spacer or Insulating Layer

In order that the reflective layer (in Fig. 3) is protected from thermal damage, and that the heat loss from the active layer is minimized, it is advantageous to insert a subbing layer which functions as an insulating layer, between the reflective layer and the active layer, and, in some cases, between the active layer and the protective layer. Typically, this is a polymeric layer. Polymethylmethacrylate and polycarbonate layers have been used satisfactorily. Refractory materials such as silicon dioxide and zinc sulphide have also been used satisfactorily.

Anti-reflection Coating

It is also useful to provide a subbing layer on a substrate that has a reflective surface, e.g., a metalized film or plate. A subbing layer of the proper thickness will serve to maximize the reflection through a recorded spot on such a substrate due to constructive interference of the incoming and reflected beam, thus maximizing the signal to noise ratio (SNR) of the medium.

Gelatin, PMMA, polycarbonate and PVA are examples of materials suitable for use a subbing layers. Layers of such materials have been solvent coated from water solutions, a toluene solution in the case of PMMA, or a toluene methylene chloride solution in the case of polycarbonate. Any plastic or refractory material may serve as a subbing layer if it has the proper optical, thermal, and solvent characteristics.

Protective Layers

A cover layer can be provided over the recording layer to protect the recording layer from scratches and to keep dust from the focal plane. Successful cover layers have been made of PMMA, PVA, polycarbonate, silicone rubber, and glass. The PMMA was solvent cast from a toluene solution. The PVA was cast from a water solution. The polycarbonate was solvent cast from a toluene/methylene chloride solution. The silicone rubber (RTV) was polymerized in place from a liquid monomer, and the glass was adhered to the recording layer using an optical adhesive. Cover layers of greater thickness (5/1000 - 47/1000 inch) comprising extruded polycarbonate sheet, cast PMMA sheet and glass have been laminated to the recording layer using optically transparent UV-curable adhesives.

If the recording beam is directed toward the active layer as shown in Fig. 3, the cover layer should be substantially transparent to the incident radiant energy beam. Recording with laser light has been performed through layers of each of the above materials. To protect the cover layer from scratching, an abrasion-resistant UV-curable coating 5-25 microns thick is used.

Recording

To record data on the medium, a beam of high-intensity radiant energy, such as laser light, is directed toward the medium as shown in Fig. 2 or 3. Radiant energy is absorbed by the photosensitive material, particularly any dye that is present, until there is sufficient energy to activate the exothermic decomposition of the metal azide.

Heat and gases released during the decomposition reaction blow a hole in the photosensitive material, which can later be read as part of a binary data pattern. When a dye is present, the reaction leaves a light area on a dark field.

In tests of recording media according to the present invention, it has been possible to produce spots as small as 0.6 microns in diameter.

The following examples describe several specific media according to the present invention.

EXAMPLE 1

Cupric azide can be formed in bulk and then dissolved in aqueous ammonia, mixed with a binder and solvent coated to form a homogeneous active layer on a substrate. Cupric azide and silver azide can be used in this way.

The cupric azide is formed stochiometrically by mixing aqueous solutions of sodium azide and cupric sulfate. 3.2 grams of cupric sulfate are dissolved in 50 ml water and added to a solution of 2.6 grams of sodium azide dissolved in 50 ml water. Upon addition, a reddish brown precipitate of cupric azide is formed. The mixture is stirred for five minutes and then filtered. The cupric azide precipitate is then dissolved in 100 ml or less of aqueous ammonia. A film of the cupric azide is formed by mixing 2 ml of the above solution with 8 ml of a 2% solution of a gelatin in water. Five drops of a surfactant, such as Kodak's Photoflo, are added to this mixture. The mixture is poured on a 4" x 5" glass plate and spun at 1900 RPM until dry. A clear thin film of cupric azide in a gelatin binder results. The film is approximately 0.25-0.5 microns thick.

EXAMPLE 2

Cupric azide can also be made in situ by spin coating a film of cupric sulfate in a binder on a suitable substrate. Four grams of cupric sulfate and 2 grams of gelatin are dissolved in 100 ml of water. One drop of a surfactant, such as Kodak's Photoflo, is added to this solution. This solution is poured on a 4" x 5" glass plate and spun at 1000 RPM for five minutes. The resulting plate is then immersed in a 2% methanol solution of sodium azide for five minutes. The plate is removed from the bath and washed with water and spun dry.

EXAMPLE 3

Lead azide is made in situ in a manner similar to that of cupric azide. Four grams of lead acetate and 2 grams of gelatin are dissolved in 100 ml water. A drop of a surfactant, such as Kodak's Photoflo, is added. The solution is coated on a 4" x 5" glass plate and spun for five minutes. The dry plate is then immersed in a 2% solution of sodium azide in methanol for five minutes. The plate is washed with water and spun dry.

EXAMPLE 4

Silver azide can also be made in situ. Four grams of silver nitrate and 2 grams of gelatin are dissolved in 100 ml water and 1 drop of a surfactant, such as Kodak's Photoflo, is added. This solution is poured on a 4" x 5" glass plate and spun at 1000 RPM for five minutes. The plate is then immersed in a 2% sodium azide in methanol solution for five minutes. The plate is washed in water and spun dry. The silver azide is formed as a homogeneous mixture in the gelatin binder.

EXAMPLE 5

The cupric azide formed in Example 1 can be coated on other substrates. A PMMA or polycarbonate sheet 1 mm thick is prepared for coating by washing with methanol while rotating at 2300 RPM. The material comprising the photosensitive layer is made by mixing 8 mls of a 2% aqueous polyethylene glycol solution with 2 ml of a 2% cupric azide solution in aqua ammonia. This mixture is poured on the PMMA substrate and spun at 1900 RPM for 10 minutes. After drying, the plate is coated with a 2% solution of IR 125 dye in methanol and spun at 1900 RPM for 3 minutes. An insulating subbing layer is then applied by vacuum coating the plate with zinc sulphide until a zinc sulphide layer 0.2 micron thick is created. A reflective layer may then be provided by vacuum depositing an aluminum layer approximately 2,000 angstroms thick. A 0.5 micron thick protective layer of zinc sulphide is then deposited over the aluminum. An incident laser beam records on this medium through the PMMA or PC substrate layer.

EXAMPLE 6

Single layer azide-dye combinations can be formed by a slight modification of the procedures described in Examples 2, 3 and 4. The layer is formed by dissolving 2 grams of dye, such as rose bengal, with 2 grams of sodium azide in 100 ml of methanol. A plate coated with one of the previously described metal salt layers is then immersed in the methanol solution, and then spun dry.

EXAMPLE 7

The active layer can be applied to a substrate by a vacuum deposition technique employing resistance heating or sputtering. These techniques eliminate the need to use a binder material.

A 4" x 5" glass plate, one millimeter thick, is placed in a vacuum chamber with two resistance heated boats. The first boat contains cuprous chloride, the second contains potassium azide. After the chamber is evacuated to 10^{-6} torr, current to the first boat is adjusted to deposit a layer of cuprous chloride 100 angstroms in thickness, at 20 angstroms per second. Next, current is supplied to the second boat to deposit 100 angstroms of the potassium azide, which reacts instantly to form cuprous azide and potassium chloride on the substrate. Current is then applied to the first boat and the procedure repeated until three to five layers are deposited. The resulting medium has an active layer 0.6 to 1.0 micron thick.

Dye and subbing layers are provided by solvent coating. One or more such layers can be solvent coated on the substrate before vacuum deposition. Or, such layers can be solvent coated over an azide layer previously formed by vacuum deposition.

EXAMPLE 8

It is also possible to use vacuum deposition to form a single active layer containing both a metal azide and a dye.

The procedure of Example 7 is repeated in a vacuum chamber equipped for sputtering. In this case, three boats or "targets" are provided. A dye, such as rose bengal, occupies the third boat.

To deposit the dye, a cathode is heated causing it to emit electrons which are accelerated through argon gas, at a negative pressure, in the chamber. The dye target is negatively biased to attract argon ions formed in the chamber. The ions strike the dye with sufficient energy to eject that substance from the target and onto the substrate.

The cuprous chloride and potassium azide can be deposited by resistance heating as described in Example 7 or by sputtering, i.e., in the same manner that dye is deposited in this example. The dye is preferably deposited at about the same rate as the other substances, i.e., at about 20 angstroms per second, so that equal amounts of the three substances are deposited. The three substances are deposited in repeated, alternating applications, until a single 0.6 to 1.0 micron layer is formed. The resulting layer is a substantially uniform dispersion of cuprous azide, potassium chloride, and dye.

EXAMPLE 9

Media can be formed by yet another vapour deposition technique.

A thin metal film of lead, silver, or copper is converted to metal azide. The film, of 0.5 micron thickness, is exposed to hydrazoic acid vapour in a closed chamber for 8 hours. The resulting film includes homogeneous metal azide. In some instances, the film would then be coated with a suitable dye, such as rose bengal or IR 125, as described in previous examples.

EXAMPLE 10

Polycarbonate of thickness 10/1000 inch is metallized with 1000 Angstroms of aluminum or gold. A spacer layer of thickness about 0.01-0.05 microns is spin-coated onto the metal layer. A binder layer 0.1-0.5 micron thick consisting of 8 ml 2% aqueous polyethylene glycol and 2 ml copper azide dissolved in aqueous ammonia is spin-coated onto the spacer layer. The ammonia evaporates during spin-coating, leaving a layer of polyethylene glycol containing a dispersion of cupric azide. A solution if IR125, 2% in methanol, is spin-coated onto the binder to give an absorbance of 1 to 2. U.V. curable adhesive is spin-coated onto the dye layer, and then a transparent substrate (PC) of thickness 10/1000 inch to 47/1000 inch is laminated under pressure to the multilayer and U.V. cured.

The laminated material so prepared acted satisfactorily as an optical recording medium, using incident low intensity laser radiation from a semi-conductor laser diode.

We have shown and described the preferred embodiments of our invention. It will be apparent to those skilled in the art that changes may be made without departing from our invention in its broader aspects. We, therefore, intend the appended claims to cover all such changes and modifications as follow in the true spirit and scope of the invention.

WE CLAIM:

1. A recording medium comprising a photosensitive material which contains a metal azide.

2. The recording medium of claim 1 wherein the photosensitive material comprises an intimate mixture of homogeneously dispersed metal azide and dye molecules.

3. A recording medium comprising:

a substrate material;

a photosensitive material consisting essentially of an energy absorptive dye and a metal azide dispersed in an inert binder; and

a transparent protective covering.

4. The recording medium of claim 3 in which the metal azide is selected from the group consisting of cupric azide, lead azide, and silver azide and mixtures thereof.

5. The recording medium of claim 3 in which the energy absorptive dye is selected from the group consisting of erythrosin, erythrosin B, rhodamine 6G, sudan 111, rose bengal, IR 125 and mixtures thereof.

6. The recording medium of claim 3 in which the binder is formed from a 1.5-2.5% solution of gelatin in water.

7. The recording medium of claim 3 in which the substrate material is selected from the group consisting of glass, polymethylmethacrylate, polyester, polyvinylacetate and polycarbonate, and any such materials coated with a reflective material.

8. The recording medium of claim 3 in which a subbing layer is provided between the photosensitive material and substrate.

9. The recording medium of claim 8 in which the subbing layer is selected from the group consisting of polyvinyl alcohol, polymethylmethacrylate, gelatin and mixtures thereof.

10. The recording medium of claim 3 in which the transparent covering is selected from the group consisting of polymethylmethacrylate, polyvinyl alcohol, polycarbonate, silicone rubber and glass.

11. A recording medium comprising:
a substrate material;
and a photosensitive material consisting essentially of
(1) an energy absorptive dye and
(2) an explosive material,
said explosive material having an appropriate explosive decomposition temperature for use in optical recording medium with low intensity laser incident energy, and being capable of emitting significant quantities of energy upon explosive decomposition.

12. The recording medium of claim 11 wherein said explosive material is a primary explosive.

13. The recording medium of claim 12 wherein said explosive material has an explosive decomposition temperature in the approximate range $100^{o}C-350^{o}C$.

14. The recording medium of claim 12 wherein said explosive material has an explosive decomposition temperature in the approximate range $150^{o}-250^{o}C$.

15. The recording medium of claim 14 wherein said explosive material is a transition metal azide.

16. The recording medium of claim 11 wherein the explosive material is cupric azide, lead azide or silver azide.

17. The recording medium of claim 11 wherein said explosive material is a metal azide selected from the group consisting of lithium azide, calcium azide, zinc azide, cadmium azide, barium azide, mercurous azide, mercuric azide, trichlorotitanium azide, strontium azide, nickelous azide and manganous azide.

18. The recording medium of claim 11 wherein the explosive material is a diazonium salt.

19. The recording medium of claim 18 wherein the explosive material is benzene diazonium nitrate or benzene diazonium perchlorate.

20. The recording medium of claim 11 wherein the explosive material is dispersed in an inert binder.

21. The recording medium of claim 11 wherein the energy absorptive dye is an infrared absorbing dye of the polymethine class or squarylium class.

22. The recording medium of claim 21 wherein the dye is a dicarbocyanine or a tricarbocyanine

23. The recording medium of claim 12 wherein the dye has an infrared radiation absorption capacity in the range 750 nm - 1100 nm, to match the wavelength of semi-conductor diode laser emission.

24. The recording medium of claim 11 wherein the energy absorptive dye sensitizes the photosensitive material to the output of an argon ion laser.

25. The recording medium of claim 11 wherein the energy absorptive dye sensitizes the photosensitive layer to ultraviolet radiation in the wavelength range 250-350 nm.

26. The recording medium of claim 11 wherein the energy absorptive dye sensitizes the photosensitive layer to visible light radiation in the wavelength range 350-750 nm.

27. The recording medium of claim 24 wherein the dye is selected from the group consisting of erythrosin, erythrosin-B, sudan III, rhodamine 6G and rose bengal.

28. The recording medium of claim 11 further including a subbing layer interposed between the substrate material and the photosensitive material, said subbing layer consisting essentially of a heat insulating material, to reduce heat losses from the photosensitive material and to protect the substrate against thermal damage.

29. The method of recording images on a recording medium which comprises contacting a beam of laser light with a medium containing (a) a substrate material, and (b) on the substrate material, a photosensitive material comprising an energy absorptive dye capable of at least partially absorbing the incident laser light and a primary explosive material, said primary explosive material having an explosion temperature in the approximate range of 100^{o}-350^{o}C, and being capable of emitting significant quantities of energy upon explosion,

the dye and the explosive material being present in amounts sufficient that the beam causes the explosive material to react exothermically at the location of contact, form a void in the photosensitive material, thereby leaving a light area on a dark field, which area can be read by an optical readout device.

30. The method of claim 29 in which the recording medium comprises a transparent protective covering over the photosensitive material.

31. The method of claim 29 in which the substrate material is selected from the group of materials consisting of glass, polymethylmethacrylate, polyester, polyvinylacetate, polycarbonate, and any such materials plated with a reflective material.

32. The method of claim 29 in which a subbing layer is provided between the photosensitive material and substrate.

33. The method of claim 32 in which the subbing layer is selected from the group consisting of polyvinyl alcohol, polymethylmethacrylate, polycarbonate, SiO_2, ZnS and gelatin and mixtures thereof.

34. The method of claim 32 wherein the subbing layer constitutes a thermally insulating layer, to reduce heat losses from the photosensitive material and to protect the substrate against thermal damage.

35. The method of claim 30 in which the transparent covering is selected from the group consisting of polymethylmethacrylate, polyvinyl alcohol, polycarbonate, silicone rubber, and glass.

36. The method of claim 29 wherein the primary explosive material has an explosive decomposition temperature in the approximate range 150-250°C.

37. The method of claim 36 wherein the explosive material is a transitional metal azide.

38. The method of claim 37 wherein the explosive material is cupric azide, lead azide or silver azide.

39. The method of claim 29 wherein said explosive material is a metal azide selected from the group consisting of lithium azide, calcium azide, zinc azide, cadmium azide, barium azide, mercurous azide, mercuric azide, trichlorotitanium azide, strontium azide, nickelous azide and manganous azide.

40. The method of claim 29 wherein the explosive material is dispersed in an inert binder.

41. The method of claim 29 wherein the explosive material is a diazonium salt.

42. The method of claim 41 wherein the explosive material is benzene diazonium nitrate or benzene diazonium perchlorate.

43. The method of claim 29 wherein the energy absorptive dye is an infrared absorbing dye of the polymethine class or the squarylium class.

44. The method of claim 29 wherein the laser light beam is produced by a semi-conductor diode laser of wavelength in the range 750 - 1100 nm, and the infrared dye has appropriate absorption characteristics to match the laser wavelength.

45. The method of claim 29 wherein the energy absorptive dye is an ultraviolet absorbing dye capable of absorbing radiation in the wavelength range 250-350 nm.

46. The method of claim 29 wherein the energy absorptive dye is a visible light absorbing dye capable of absorbing radiation in the wavelength range 350-750 nm.

47. The method of forming a medium to record images which comprises:

providing on a substrate material, a photosensitive material which contains a metal azide.

48. The method of claim 47 comprising:

adhering a metal salt to a substrate; and

contacting the substrate with a solution of an azide salt so that the azide in solution reacts with the metal salt to leave metal azide on the substrate.

49. The method of claim 48 wherein the azide salt is an alkali metal azide.

50. The method of claim 47 comprising alternately vacuum depositing on the substrate:

a first substance selected from the group consisting of a lead halides, silver halides, cuprous halides, and mixtures thereof; and

a second substance selected from the group consisting of alkali metal azides and mixtures thereof.

51. The method of claim 50 comprising providing a dye on the substrate before the vacuum depositing.

52. The method of claim 50 comprising providing a dye on the vacuum deposited material.

53. The method of claim 50 comprising vacuum depositing a dye to provide a homogeneous dispersion of dye in intimate contact with the other vacuum deposited material.

54. The method of forming a medium to record images which comprises treating a thin metal film with hydrazoic acid vapour to provide homogeneous film of metal azide.

55. The method of forming a medium to record images, which comprises:

providing on a substrate material, a photosensitive material which contains an energy absorptive dye and a primary explosive material which has an explosive decomposition temperature in the approximate range 100°-350°C and which is capable of emitting significant quantities of energy upon explosive decomposition.

56. The method of claim 55 wherein said explosive material is a primary explosive having an explosive decomposition temperature in the approximate range 150°C-250°C.

57. The method of claim 55 wherein said explosive material is a metal azide selected from the group consisting of lithium azide, calcium azide, zinc azide, cadmium azide, barium azide, mercurous azide, mercuric azide, trichlorotitanium azide, strontium azide, nickelous azide and manganous azide.

58. The method of claim 55 wherein the explosive material is a diazonium salt.

59. The method of claim 55 wherein the energy absorptive dye is an infrared absorbing dye of the polymethine class or the squarylium class.

60. The method of claim 55 wherein the dye has an infrared radiation absorption capacity in the range 750 - 1100 nm, to match the wavelength of semi-conductor diode laser emission.

61. The method of claim 55 wherein the energy absorptive dye is an ultraviolet absorbing dye capable of absorbing radiation in the wavelength range 250-350 nm.

62. The method of claim 55 wherein the energy absorptive dye is a visible light absorbing dye capable of absorbing radiation in the wavelength range 350-750 nm.

63. The method of claim 55 wherein said explosive material is a transition metal azide.

64. The method of claim 63 wherein said explosive material is cupric azide, lead azide or silver azide.

AMENDED CLAIMS
[received by the International Bureau
on 7 March 1988 (07.03.88);
original claim 54 cancelled; claims 1 and 48 amended;claims 55-64
renumbered as 54-63 (4 pages)]

1. A recording medium comprising a photosensitive material which comprises a metal azide and dye molecules.

2. The recording medium of claim 1 wherein the photosensitive material comprises an intimate mixture of homogeneously dispersed metal azide and dye molecules.

3. A recording medium comprising:

a substrate material;

a photosensitive material consisting essentially of an energy absorptive dye and a metal azide dispersed in an inert binder; and

a transparent protective covering.

4. The recording medium of claim 3 in which the metal azide is selected from the group consisting of cupric azide, lead azide, and silver azide and mixtures thereof.

5. The recording medium of claim 3 in which the energy absorptive dye is selected from the group consisting of erythrosin, erythrosin B, rhodamine 6G, sudan 111, rose bengal, IR 125 and mixtures thereof.

6. The recording medium of claim 3 in which the binder is formed from a 1.5-2.5% solution of gelatin in water.

7. The recording medium of claim 3 in which the substrate material is selected from the group consisting of glass, polymethylmethacrylate, polyester, polyvinylacetate and polycarbonate, and any such materials coated with a reflective material.

8. The recording medium of claim 3 in which a subbing layer is provided between the photosensitive material and substrate.

providing on a substrate material, a photosensitive material which contains a metal azide.

48. A method of forming a medium to record images which comprises:

adhering a metal salt to a substrate; and

contacting the substrate with a solution of an azide salt so that the azide in solution reacts with the metal salt to leave metal azide on the substrate.

49. The method of claim 48 wherein the azide salt is an alkali metal azide.

50. The method of claim 47 comprising alternately vacuum depositing on the substrate:

a first substance selected from the group consisting of a lead halides, silver halides, cuprous halides, and mixtures thereof; and

a second substance selected from the group consisting of alkali metal azides and mixtures thereof.

51. The method of claim 50 comprising providing a dye on the substrate before the vacuum depositing.

52. The method of claim 50 comprising providing a dye on the vacuum deposited material.

53. The method of claim 50 comprising vacuum depositing a dye to provide a homogeneous dispersion of dye in intimate contact with the other vacuum deposited material.

54. The method of forming a medium to record images, which comprises:

providing on a substrate material, a photosensitive material which contains an energy absorptive dye and a primary explosive material which has an explosive decomopsition temperature in the approximate range 100-350 degrees C and which is capable of emitting significant quantities of energy upon explosive decomposition.

55. The method of claim 54 wherein said explosive material is a primary explosive having an explosive decomposition temperature in the approximate range 150-250 degrees C.

56. The method of claim 54 wherein said explosive material is a metal azide selected from the group consisting of lithium azide, calcium azide, zinc azide, cadmium azide, barium azide, mercurous azide, mercuric azide, trichlorotitanium azide, strontium azide, nickelous azide and manganous azide.

57. The method of claim 54 wherein the explosive material is a diazonium salt.

58. The method of claim 54 wherein the energy absorptive dye is an infrared absorbing dye of the polymethine class or the squarylium class.

59. The method of claim 54 wherein the dye has an infrared radiation absorption capacity in the range 750-1100 nm, to match the wavelength of semi-conductor diode laser emission.

60. The method of claim 54 wherein the energy absorptive dye is an ultraviolet absorbing dye capable of absorbing radiation in the wavelength range 250-350 nm.

61. The method of claim 54 wherein the energy absorptive dye is a visible light absorbing dye capable of absorbing radiation in the wavelength range 350-750 nm.

62. The method of claim 54 wherein said explosive material is a transition metal azide.

63. The method of claim 62 wherein said explosive material is cupric azide, lead azide or silver azide.

STATEMENT UNDER ARTICLE 19

Claim 1 has been amended to change "contains a metal azide" to "comprises a metal azide and dye molecules".

Claim 48 has been amended to place it in independent form by amending the preamble to read "A method of forming a medium to record images which comprises".

Claim 54 has been deleted and the remaining claims renumbered and their dependency amended.

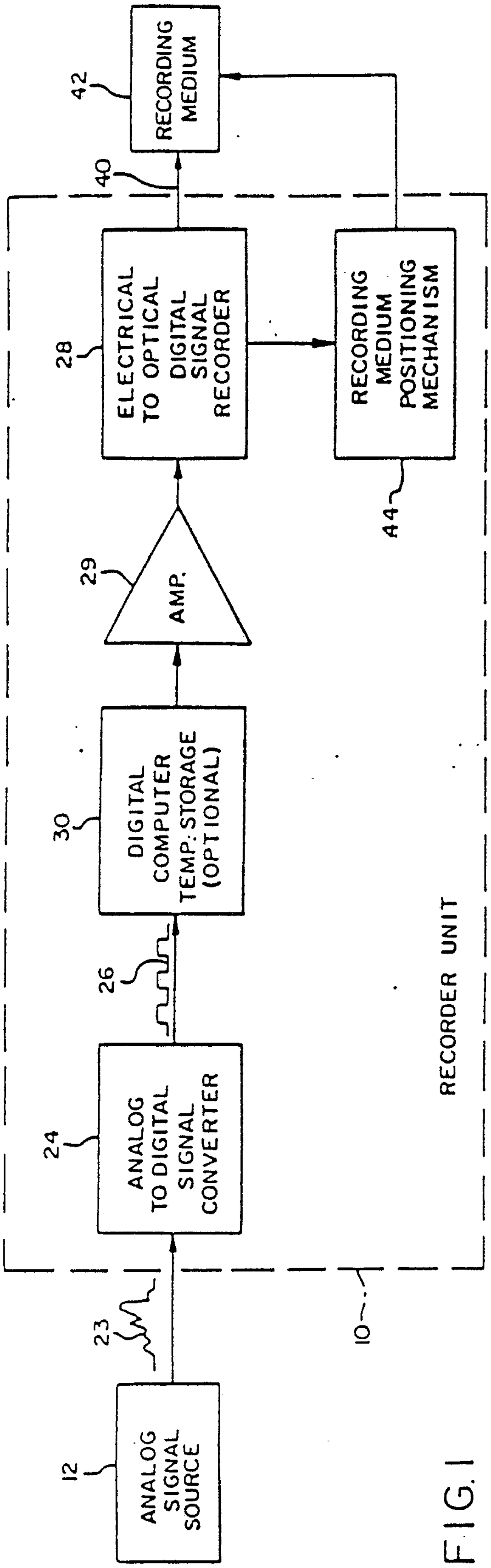


FIG. 1

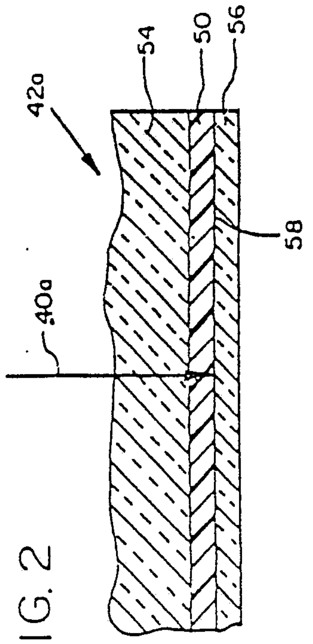


FIG. 2

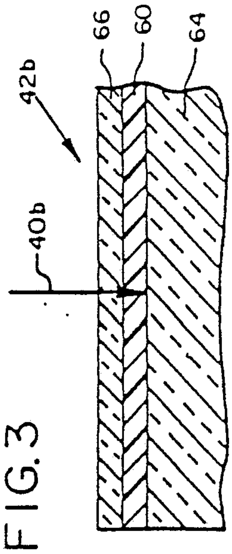


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/02404

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT CL4 G03C 1/72, 1/76, 5/16; G01D 15/14, 15/34
US CL 430/141, 157, 167, 168, 176, 177, 196, 270

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	346-766, 135.1; 427-248.1, 249, 250, 252, 253; 430-141, 155, 157, 158, 160, 162, 167, 168, 171, 176, 177, 196, 197, 269, 270, 271, 273, 290, 320, 321, 346, 495, 616, 945

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
E, X Y	US,A, 4,622,284 (WEST) 11 NOVEMBER 1986. See the entire document.	1-17,20,23-40 44-49,55-57 60-64 1-64
X Y	US,A, 3,778,269 (WIEGAND) 11 DECEMBER 1973. See the entire document.	1,47,54 1-64
X Y	US,A, 3,298,833 (GAYNOR) 17 JANUARY 1967. See the entire document.	1,47 1-64
X Y	US,A, 3,316,088 (SCHAFFERT) 25 APRIL 1967. See the entire document.	1,47 1-64
X Y	US,A, 2,703,283 (EGGERT) 01 MARCH 1955. See the entire document.	1,47 1-64
Y	US,A, 4,230,939 (de BONT) 28 OCTOBER 1980. See the entire document.	1-64
Y	US,A, 4,032,691 (KIDO) 21 MARCH 1975. See the entire document.	28,32-34, 47-53

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 18 DECEMBER 1986	Date of Mailing of this International Search Report [2] 13 FEB 1987
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] CHARLES L. BOWERS, JR.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
Y	US,A, 4,069,487 (KASAI) 17 JANUARY 1978. See the entire document.	3,30,35
X Y	JAPAN, B, 58-179693 (AKIYAMA), 20 OCTOBER 1983. See the entire document.	11-14,18,19,20 23-25,29,31, 40-42,44,46,55 56,58,60,62 1-64
Y	US,A, 3,515,554 (ROBILLARD) 02 JUNE 1970. See the entire document.	1-64
Y	US,A, 4,508,811 (GRAVESTEIJN) 02 APRIL 1985. See the entire document.	11,21,23,29,43 44,55,58-64
Y	US,A, 4,547,444 (BELL) 15 OCTOBER 1985. See the entire document.	11,21-23,29,43 44,55,58-60
Y	US,A, 4,599,298 (FISCH) 08 JULY 1986. See the entire document.	47-53
Y	US,A, 4,455,364 (SASA) 19 JUNE 1986. See the entire document.	47-53
Y	US,A, 4,268,541 (IKEDA) 19 MAY 1981. See entire document.	47-53
Y	US,A, 3,811,884 (INOUE) 21 MAY 1974. See entire document.	47-53
A	US,A, 3,787,210 (ROBERTS) 22 JANUARY 1974. See entire document.	1-64
A	US,A, 4,023,185 (BLOOM) 10 MAY 1983. See entire document.	1-64
A	US,A, 4,404,656 (CORNET) 13 SEPTEMBER 1983. See entire document.	1-64
Y	N, J of the Society of Motion Pictures and Television Engineers, Vol. 83, No. 7, issued JULY 1974. (BERG) High Resolution Graphics Using a HeCd Laser to Write on Kalvar Film, See pages 588-99.	1-64
Y	N, Optical Engineering, Vol. 15, No. 2, issued MARCH/APRIL 1976, (BARTOLINI) Optical Recording Media, see pages 99-108.	1-64
Y	N, The Journal of Photographic Science, Vol. 19, issued 1971, Possible Use of Certain Metallic Azides for the Development of a Field Controlled Dry Photographic Process, see pages 25-39.	1-64

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V.☐ **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE** [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☒ **OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING** [11]

This International Searching Authority found multiple inventions in this international application as follows:

I - Recording Medium: Claims 1-28
II - Method of Recording with Laser: Claims 29-46
III - Method of making Recording Medium Utilizing Various Procedures:
Claims 47-64

1.☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone practice

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

ATTACHMENT TO FORM PCT/ISA/210, PART VI. 1

TELEPHONE APPROVAL:

In a telephone conference on December 17, 1986 with the Examiner, Mr. Douglas Price, attorney for applicants, agreed to pay for the other two inventions described hereafter which were not searched in a national application with some inventive entity, namely Groups I and III, wherein the elected invention in the national application, 06/585,175, was Group II. Accordingly, Mr. Price authorized the Commissioner to charge Deposit Account No. 06-1358, the required $280.00 for the additional inventions searched.

Counsel advised that he has no right to protest for any group not paid for and that any protest must be filed no later than 15 days from the date of mailing of the search report (Form 210).

REASONS FOR HOLDING LACK OF UNITY OF INVENTION:

I is classified 430/167 and can be used in a different method of use than in II to include use in making photoresist image or lithographic printing plate not requiring use of laser as well as in a different method of manufacture, than in III to include thermal transfer from a receptor surface or liquid coating procedure of use without a substrate, i.e., one integral layer. II is classified in 430/290 and III is classified in 430/168.

TIME LIMIT FOR FILING A PROTEST:

Applicant is hereby given 15 days from the mailing date of this Search Report in which to file a protest of the holding of lack of unity of invention. In accordance with PCT Rule 40.2 applicant may protest the holding of lack of unity only with respect to the group(s) paid for.