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WO A1 87/00341 US 4101976
Optics Communications Vol. 51 No. 6 October 1984 pages 412 to 415
Chemical Physics Letters Vol. 94 No. 5 February 1983 pages 483 to 487
Molecular physics Vol. 45 No. 1, 1982 pages 113 to 127

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G2J
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G02F G11C

(54) Method of optically recording and reading information

(57) A method of optically recording and reading items of information uses a recording material 3 which contains at least one radiation-sensitive compound having at least one inhomogeneously dispersed absorption band in the UV and/or visible and/or IR spectral region. Under the action of narrow-band laser light 8 with at least one frequency lying within said absorption band and an externally adjustable electrostatic, magnetic or pressure field, the compound undergoes a change in absorption behaviour, such that, by adjustment to another field strength of the electrostatic, magnetic or pressure field, further changes in the absorption behaviour, can be produced and therefore additional items of information recorded. These changes, can be read off again on reproducing the field strengths at the time of recording. The items of information are recorded and read in the form of holograms. The change in the absorption behaviour is as a result of photophysical or photochemical hole burning.

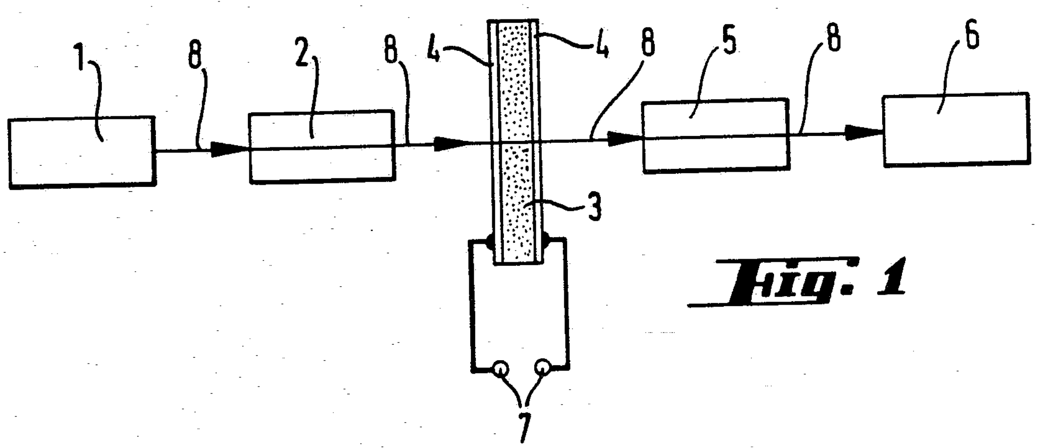

Fig. 1

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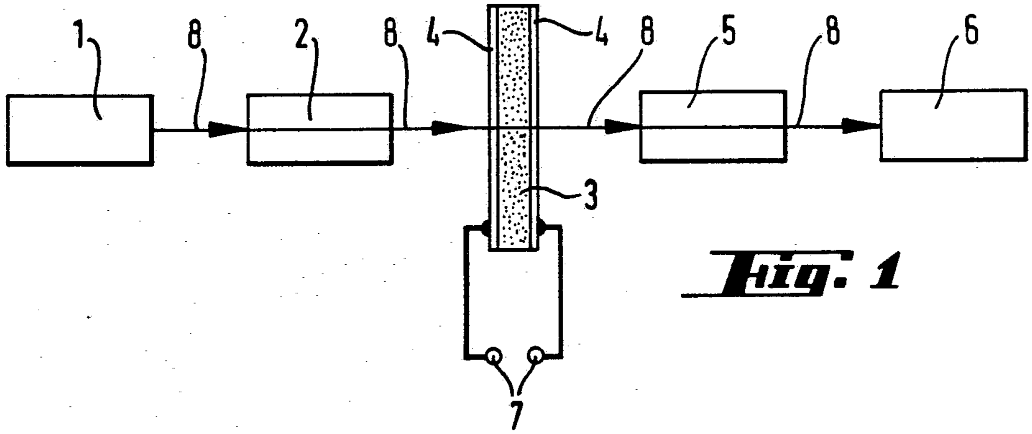


Fig. 1

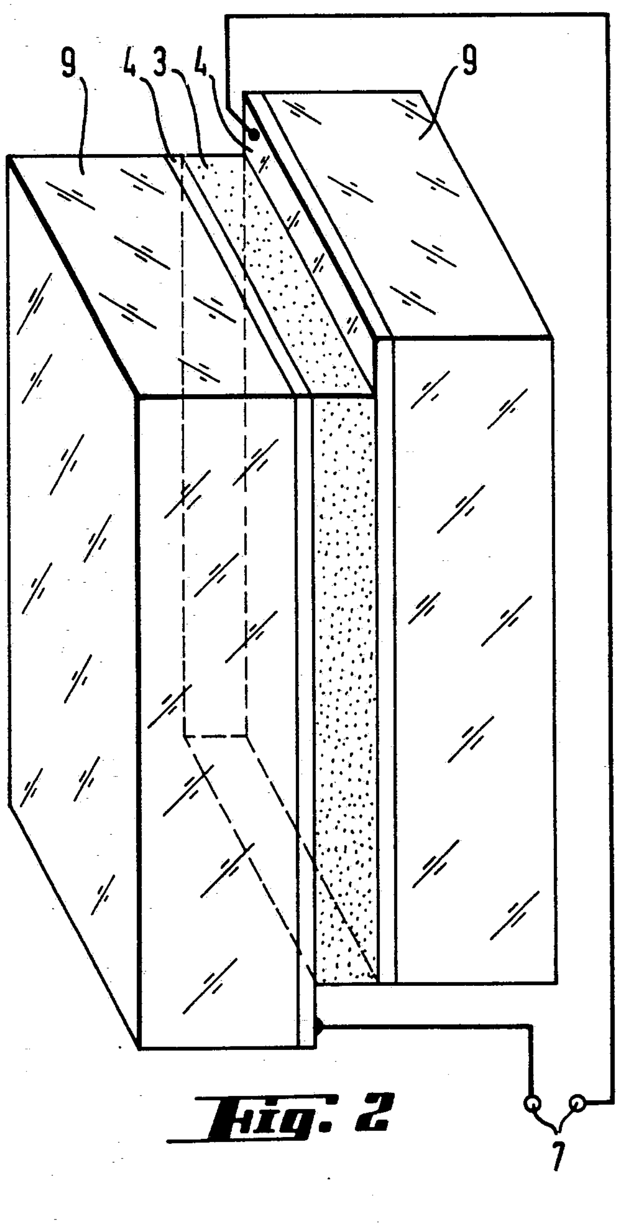


Fig. 2

Fig. 3a

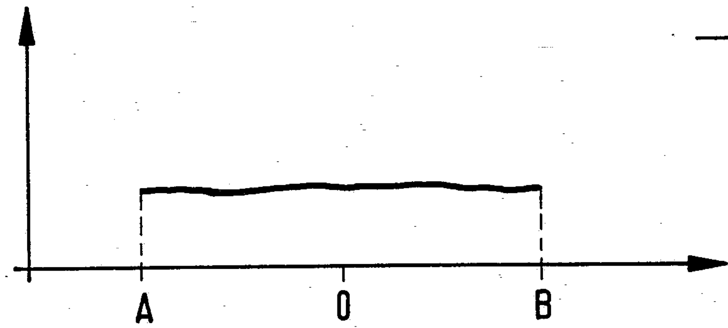


Fig. 3b

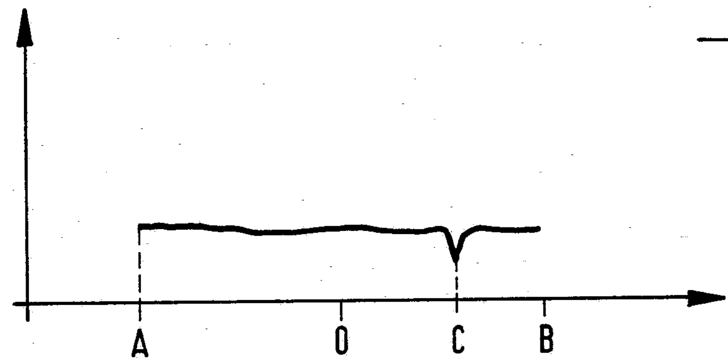


Fig. 3c

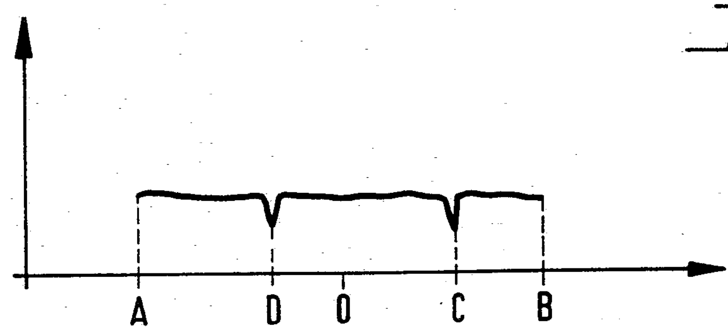
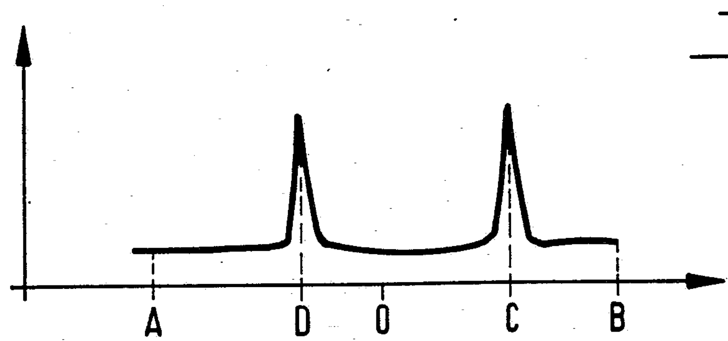
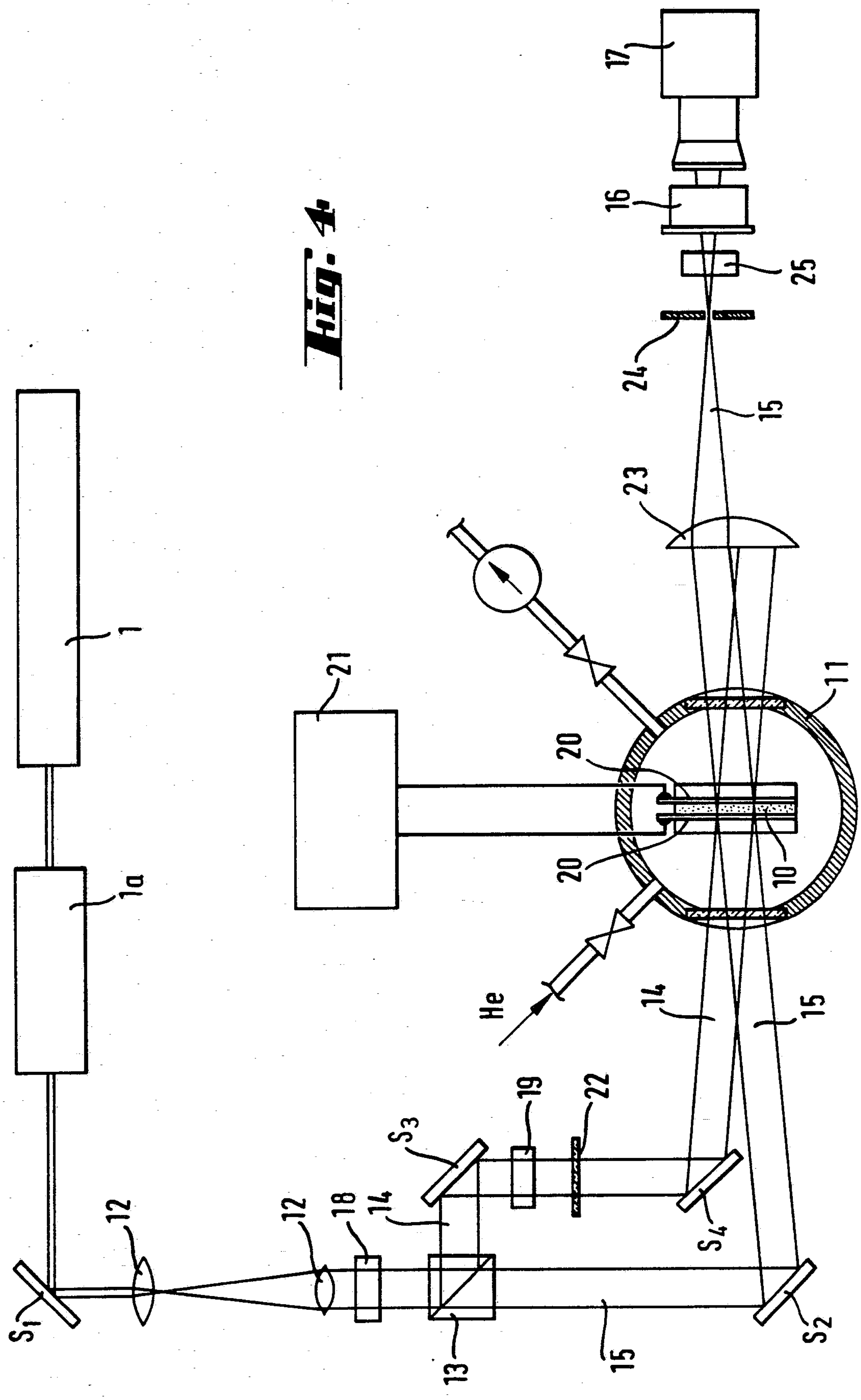


Fig. 3d




1
1a
S1
12
12
18
13
14
15
S2
S3
19
22
S4
14
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He
20
20
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23
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16
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Fig. 4

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Method of optically recording and reading information

The present invention relates to a method for recording and reading items of information in the form of holographically generated optical changes in a recording material which contains at least one radiation-sensitive compound having at least one inhomogeneously dispersed absorption band in the UV and/or visible and/or IR spectral region.

The recording of data or image information in the form of interference patterns (termed a hologram) by means of coherent laser light rays on radiation-sensitive material is known to those skilled in the art and is described, for example, in Optical Holography by P. Hariharan, Cambridge University Press 1984, in particular on pages 1-2. If the hologram is then illuminated in a second step with coherent laser light from the same direction as the reference wave was incident during the recording, diffraction at the interference patterns produces two deflected light beams, of which one generates a three-dimensional, real image behind the hologram and the other generates a three-dimensional virtual image in front of the hologram. The virtual image can be observed directly with the eye, its aspect changing with the position of the observer in the same way as the aspect of the object itself. With a fixed geometrical arrangement, this method permits only one single image to be recorded per surface element of the recording material.

It is further known, for example, according to US Patent No. 4,101,976 that radiation-sensitive compounds in a material (matrix) which have at least one inhomogeneously dispersed absorption band are converted into a new, photochemically or photophysically altered state by irradiation with laser light of narrow bandwidth at low temperatures. These optical changes should expediently be narrow-band changes in order to ensure the desired high spectral resolution. It is consequently possible to burn in a large number of spectral holes at the same geometrical position, which are independent of each other within the inhomogeneously dispersed absorption band of a radiation-sensitive compound at different wavelengths and then to detect them again at the corresponding wavelengths. In this manner, items of information in digital form (often termed bits = binary numbers) can be stored at a particular point in the material by assigning individual bits to one spectral hole each so that a very large amount of information is stored in a certain volume of the material. The photochemical mechanism of this type of optical bleaching involves only those molecules which absorb at the laser frequencies employed; the remaining molecules in the material which absorb at other frequencies remain unchanged because they do not take part in the photo-induced reaction.

From the above US Patent No. 4,101,976 (column 4, lines 27-30) it may be inferred that the recording of items of information can also be carried out holographically.

Furthermore, it is known, for example, from Chemical Physics Letters 94 (1), pages 483-487 (1983) that such spectral holes generated by suitable laser light can be altered under the influence of an electrostatic field (Stark effect) in such a manner that their absorption depth decreases and their spectral width is extended. Similar effects can also be achieved if an electrostatic field applied during the burning of the spectral hole is subsequently changed or reduced. In addition, according to Molecular Physics 45, No. 1, pages 113-127 (1982) it is also known that magnetic fields exert a similar influence on spectral holes and that, for example, according to Optics Communications 51, pages 412-416 (1984) spectral holes changed correspondingly under the influence of pressure (as hydrostatic pressure or as sound waves). The spectral holes are produced again if the same field strength is established during the detection which existed during the recording. In this manner, several bits in the form of photochemical holes can also be recorded at one point in a matrix, and according to this literature reference a laser with a fixed wavelength may be used.

It has now been found that several holograms can be stored as spectral holes in a suitable recording material if, under the influence of variable external fields, several different holograms are recorded at the same position in the recording material and at the same laser wavelength and are then read. Surprising in this connection is the fact that the recorded holograms can be made visible again with good selectivity by simple reconstruction of the original field strength although the spectral holes change only their form and depth as a result of the influence of different external fields. This is all the more surprising since the same type of molecules can be used for different information, which has been recorded with different external fields, as storage material (for recording and reading) without the burnt-in holes completely disappearing; as a result of this, the different items of information can be recorded and read independently of each other.

The invention accordingly relates to a method of optically recording and reading items of information in a recording material which contains at least one radiation-sensitive compound having at least one inhomogeneously dispersed absorption band in the UV and/or visible and/or IR spectral region, which compound, under the action of narrow-band laser light with at least one frequency lying within said absorption band and under the action of an externally adjustable electrostatic, magnetic or pressure field, undergoes a change in the absorption behaviour, such that by adjustment to another field strength of the electrostatic, magnetic or pressure filed, further changes in the absorption behaviour can be produced and therefore additional items of information recorded, which changes however, can be read off again on reproducing the field strengths at the time of recording, wherein the items of information are recorded and read in the form of holograms.

An electrostatic field is preferred as externally adjustable field.

Particularly suitable are radiation-sensitive compounds which absorb in the UV and/or visible and/or near IR spectral region, quite particularly, however, in the visible and/or near IR spectral region.

The near IR spectral region is to be understood as meaning the region between 0.78 µm and 2 µm.

The radiation-sensitive compound may be present in the recording material (matrix) which is suitable according to the invention for example in a quantity of 0.001 to 30% by weight, referred to the recording material, preferably of 0.01 to 10% by weight, in particular, however, of 0.01 to 0.5% by weight. The optimum concentration depends in particular on the compound employed, on the thickness of the recording material and the laser frequency which is used to produce the hologram.

As a result of the action of narrow-band laser light of a particular frequency, certain molecules of said radiation-sensitive compound undergo, as a result of the process of photophysical or photochemical hole burning, a change in the absorption profile of the inhomogeneously dispersed band affected by the laser frequency. Information bits may therefore be recorded with a laser of particular frequency at various values of the externally applied field (electrostatic, magnetic or pressure field) and later read again by adjusting to the field strength corresponding to the recording operation. Changes in the absorption behaviour of the radiation-sensitive compounds may be coupled physically also with changes in the refractive index of the recording material and the diffraction efficiency of the holograms may be influenced by the two effects.

The area of the surface irradiated by the laser can be from a few micrometers to several centimeters. The holograms on small surfaces are read with the aid of optical instruments.

At low temperature, the lifetime of such radiation-induced information bits is in general in the order of magnitude of years so that said items of information may be regarded as stable.

Examples of compounds which are suitable according to the invention and which may undergo photophysical or photochemical reactions as a result of selective irradiation, are substances which may be changed, for example, according to Phys. Bl. 41 (1985), No. 11, pages 363-369, by one- or two-photon processes, in particular proton transfer or tautomerism reactions being suitable for one-photon processes and, for example, photochemical decompositions and photoionization being suitable for two-photon reactions. The change in the position or orientation of molecules of the radiation-sensitive compound in the matrix, for example indirect reorientation of adjacent matrix molecules, also falls within the concept of photophysical hole burning. An example of a proton transfer reaction is the quinizarin molecule, whose intramolecular hydrogen bond is broken by suitable irradiation and forms an intermolecular bridge to the matrix. As a result of this, a spectroscopic shift by a few hundred wavenumbers can be generated so that the photoproduct produced lies outside the inhomogeneously dispersed absorption band of the starting substance in relation to its absorption. An example of a phototautomerization is phthalocyanine and an example of a photochemical reaction is dimethyl-s-tetrazine.

Suitable radiation-sensitive compounds according to the invention are, for example, porphin derivatives, such as porphyrine, deuterized porphyrine, tetraphenylporphyrine, 7,8-dihydroporphyrine (chlorin), and also porphyrazines, such as unsubstituted or substituted phthalocyanines, and also quinazirine, α-diketones, such as benzil, camphorquinone or biacetyl, oxazines, such as the iminium perchlorate of 3,7-bisethylamino-2,8-dimethylphenoxazine, and also tetrazines, such as dimethyl-s-tetrazine or diphenyl-s-tetrazine, spiropyrans, isoimidazoles, azirins, and also compounds which are known to those skilled in the art as laser dyes.

Compounds which can be changed photochemically by cis-trans isomerization, such as maleic acid, fumaric acid or crotonic acid are also suitable.

Particularly preferred compounds are porphin derivatives, porphyrazines, quinizarin, α-diketones and tetrazines.

For recording the items of information in the recording material suitable according to the invention use is expediently made of spectrally pure laser sources. In this process, the energy radiation is directed, focused or unfocused, at the surface of the recording material to be marked in accordance with the form of the information to be impressed, a spectal change occurring at the irradiated position.

Examples of such laser sources are solid-state pulsed lasers, such as alexandrite lasers, ruby lasers or frequency multiplied Nd:YAG lasers, pulsed lasers with additional equipment, such as pulsed dye lasers or Raman shifters, furthermore continuous-wave lasers which have or do not have pulse modifications (Q-switch, mode-locker), for example based on CW Nd:YAG laser with frequency multiplier, continuous dye laser or CW ion lasers (Ar, Kr), and also pulsed metal vapour lasers, for example, Cu vapour lasers or Au vapour lasers, or semiconductor lasers with small spectral bandwidth, in particular, so-called single-mode lasers.

In the case of the solid-state and gas lasers mentioned the use of additional equipment to reduce the bandwidth, for example prisms, grids and etalons, inside the laser resonator is advantageous.

Continuous wave lasers, for example, those listed in the table below are preferred in addition to other commercial lasers suitable according to the invention.

Table

Type/representative	Commercial example	Main wavelength (subsidiary wavelengths) [nm]
Pulsed laser with additional equipment such as . dye laser	Lambda Physik FL 2002	approx. 300-1000
CW laser (with pulse modification) . Nd:YAG (Q-Switch,2ω)	Lasermetrics (9560QTG)	532
. Argon (mode-locked)	Spectra-Physics 161	514.5/488
. Helium-Neon	PMS LSTP 0010	632.8/543.8/594.1/612/1152
Pulsed metal vapour lasers . Cu vapour laser	Plasma-Kinetics 751	510, 578
. Au vapour laser	Plasma-Kinetics	628
. Mn vapour laser	} Oxford	534, 1290
. Pb vapour laser	} Laser CU 25	723
Semiconductor diode lasers	Sharp LT-020 MC Spectra Diode Labs, Inc. 502-2410-H1	780
Semiconductor diode lasers Array	STANTEL Type LF 100	905
CW dye laser	Coherent CR-699-21	approx. 400-900

The recording material (matrix) suitable according to the invention may be high-molecular weight organic material of natural or synthetic origin, glass, ceramic glass or a frozen liquid.

If the recording material is a high-molecular weight organic material, it may be, for example, natural resins or drying oils, but also modified natural substances, for example oil-modified alkyd resins or cellulose derivatives such as cellulose esters or cellulose ethers, and particularly completely synthetic organic polymeric plastics, i.e. plastic materials which are prepared by polymerization, polycondensation or polyaddition. From the category of these plastic materials particular mention may be made of the following: polyethylene, polypropylene, polyisobutylene, polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinylacetal, polyacrylonitrile, polyacrylic acid and polymethacrylic acid esters or polybutadiene, and also copolymers thereof, in particular ABS or EVA; polyesters, in particular high-molecular esters of aromatic polycarboxylic acids with polyfunctional alcohols; polyamides, polyimides, polycarbonates, polyurethanes, polyethers such as polyphenylene oxide, polyacetals, the condensation products of formaldehyde with phenols, the so-called phenolic plastics, and the condensation products of formaldehyde with urea, thiourea and melamine, the so-called aminoplastics; the polyaddition or polycondensation products known under the name of "epoxy resins" of epichlorohydrin with diols or polyphenols and also the polyesters used as coating resins and, in particular, both saturated, for example alkyd resins, and also unsaturated, for example maleic resins. It should be emphasized that not only the homogeneous compounds, but also mixtures of polymeric plastics and also cocondensates and copolymers, for example those based on butadiene, may be used.

High-molecular weight organic materials in dissolved form as film-forming agents are also suitable, for example linseed oil varnish, nitrocellulose, alkyd resins, phenolic resins, melamine resins, acrylic resins and urea formaldehyde resins, it being possible to employ the films obtained therefrom, for example, on transparent carriers or between two transparent carriers.

The radiation-sensitive compound suitable according to the invention is added to the high-molecular weight organic known per se, for example in a manner such that such a compound which may be in the form of master batches is mixed with this substrate using extruders, rolling mills, or mixing or grinding apparatus. The radiation-sensitive compounds may also be added before the final polymerization or crosslinking to a mixture of monomers, prepolymers, saturated or unsaturated oligomers and/or multifunctional monomers, with or without the addition of polymerization initiators so that said compounds are permanently incorporated in the matrix chemically or physically during the polymerization or crosslinking. The material obtained is then converted to the desired final form by methods known per se such as calendering, moulding, extrusion moulding, coating, casting, extrusion or injection moulding. Often it is desirable, in order to prepare nonrigid moulded bodies or to reduce their brittleness to deformation, to incorporate so-called plasticizers in the matrix materials. For example, esters of phosphoric acid, phthalic acid or sebaccic acid may be used as such. The plasticizers may be worked into the polymers before or after the incorporation of the radiation-sensitive compound.

To prepare films, the matrix materials and the radiation-sensitive compound, with or without further additives, are finely dispersed or dissolved in a common organic solvent or solvent mixture. In doing this, the procedure may be such that the individual components are dispersed or dissolved alone or even several together and only then are all the components brought together. The homogenized mixture is then applied by methods known per se to a transparent substrate and burnt in or dried, and the film obtained is then irradiated according to the invention.

The dried film may be applied to another transparent substrate or fixed between two carrier plates also before the irradiation. If the matrix material has sufficient strength, it may also be provided directly with transparent electrodes. As a result of this, the transparent carrier plates become superfluous.

If the recording material (matrix) is glass or ceramic glass, the latter are glasses and ceramic glasses which are well known to those skilled in the art and are described, for example, in Ullmann's Enzyklopädie der technischen Chemie, 4th edition, vol. 12, pages 320-323 and 361-364. Examples of these are silicate glasses, two-component silicate glasses, borate, phosphate, borosilicate, aluminosilicate and lead glasses. Glasses which are prepared by the sol-gel method can also be used according to the invention.

The recording material suitable according to the invention may also be a frozen liquid which is, for example, liquid at room temperature but solid and transparent at lower temperature. In this case, the radiation-sensitive compound is expediently dissolved in the suitable liquid, for example at room temperature, after which a solid recording material, for example in the form of a thin film, is prepared by cooling the solution obtained in a suitable cell with short path length to below the freezing point of the liquid used.

Examples of suitable liquids are alcohols, such as ethanol, and also glycols, glycerol, ether, n-alkanes, ketones, esters or amides, or mixtures of these liquids.

The recording material suitable according to the invention may also be a mixture of the liquids specified above with each other or of one or more of these liquids with a high-molecular weight organic material specified above.

For the method according to the invention, especially preferred recording materials are amorphous transparent materials.

Quite particularly preferred materials are, for example, polyacrylates, such as polymethyl methacrylate, polyethyl methacrylate, polymethyl or polyethyl acrylate, polycyanoacrylates, such as α-methyl, α-ethyl or α-isobutyl cyanoacrylate, polyethylene, polypropylene, polystyrene, polyvinylacetals, such as polyvinylbutyral, polyvinylcarbazoles or polyvinyl alcohols.

During recording and reading, the laser is adjusted to a selected position on the recording material by the method known to those skilled in the art, for example, by means of deflection using moveable mirrors, moveable prisms, electrooptical elements or by means of displacing the recording material.

The most varied types of recording can be obtained by the method according to the invention. Examples of these are: characters, data, images, bit patterns, and also the most varied items of information.

The invention may be explained in more detail below by reference to the drawings 1, 2, 3a, 3b, 3c and 3d. These individually show:

Figure 1: a schematic representation of a suitable storage device according to the invention including the means for writing and reading the information,

Figure 2: a perspective representation of the storage medium and of the electrode arrangement,

Figure 3a: the absorption behaviour of the material as a function of the applied field strength before it is exposed to the laser light,

Figure 3b: the absorption behaviour of the recording material as a function of the applied electrical field strength after it has been exposed to illumination by laser light of a fixed frequency in a particular electrical field C,

Figure 3c: the absorption behaviour of the recording material as a function of the electrical field strength after it has been exposed to irradiation with the same fixed laser frequency at two different electrical field strengths C and D,

Figure 3d: the holographic diffraction efficiency of the recording material as a function of the field strength after it has been subjected to a holographic illumination with the same fixed laser frequency at two different field strengths C and D.

If the information is recorded as holograms, the diffraction efficiency of the hologram generated in the recording material depends on the field strength. Figure 3d shows the diffraction efficiency of two holograms which were recorded at the field strengths C and D. The maxima in the field strengths C and D represent holographically stored information which stands out clearly and with a good signal/noise ratio from the zero line.

Figure 4 shows a diagrammatic representation of a recording device which can be employed according to the invention.

Figure 1 represents diagrammatically an optical storage device to which the electrical field strength is applied. The optical information storage device contains a laser light source which operates stably at one or more fixed frequencies and whose line or lines are of narrowbandwidth in relation to the inhomogeneously dispersed absorption band. It must be possible to match the light intensity of the laser to the requirements of the storage material in the write and read process. If the laser 1 operates at more than one fixed frequency, an optical filter is used to select the desired laser frequency. The laser ray 8 generated is holographically structured by a suitable structure 2. The equipment for the spatial deflection of the laser ray is not shown and is of standard construction. The storage medium 3 is situated in an electrical field by applying an external voltage 7 to a set of suitably constructed transparent electrodes 4. When laser light of fixed frequency is incident, the storage medium 3 undergoes a permanent or time-limited absorption change which is substantially reformed to the value present before the incidence of radiation by a change in the electrical field strength, but if the electrical field strength is restored appears again essentially in the form originally recorded. The optical filter 5 and a detector circuit 6 are used only during the read process.

Figure 2 shows a perspective representation of the recording material (storage medium) in the form of a film to which an electrical field can be applied by two electrodes, and the arrangement of the electrodes. This film has a dimension of 20 mm x 10 mm x 50 µm and is arranged between two transparent glass plates 9 which each carry an electrode for generating the electrical field. Said glass plates serve as carriers for the electrically conducting and optically transparent electrodes 4 vapour-deposited on the inside. The concentration of the radiation-sensitive compound is chosen so that, at the maximum of the inhomogeneously dispersed absorption band, an optical density of approximately 1 is produced. A narrow-band frequency-stabilized dye laser of a frequency which lies in the region of the inhomogeneous bandwidth is used for writing. With an incident radiation intensity of, for example, 0.2 mW/cm^2, absorption changes in the order of 0.3 optical density units can be achieved within a few seconds in the storage medium, which is situated in a cryostat at the temperature of liquid helium. The storage properties of the storage medium are substantially affected by the choice of its operating temperature. At lower temperatures, the achievable storage capacity increases. Furthermore, the storage properties depend also on the nature of the (polymer) film. Thus, for example, chlorin in a polymethyl methacrylate film exhibits a storage capacity smaller by approximately a factor of two than that of a polyvinylbutyral film. Substances or centres with good storage capacity are remarkable for the fact that in such substances the difference in the dipole moments and/or the polarizabilities between the ground state and the excited electron state used is as large as possible.

According to the items of information to be stored, the recording material is written on in each case at a fixed laser frequency with an externally applied field strength which changes stepwise, each recording and reading operation being carried out in each case at a field strength which remains constant.

If the laser light with a fixed frequency within the inhomogeneously dispersed absorption band is holographically incident on the storage medium which is situated in the applied field,the laser produces a narrow spectral hole. In this case, molecules or centres are involved which absorb the laser light of the fixed frequency in said field of a particiular magnitude. The selection of these molecules affected by the bleaching out method is determined, inter alia, by the magnitude of the applied field strength. The change in absorption behaviour produced in the storage material may be either permanent or time-limited. Further information storage processes may be carried out after changing said electrical field on the same principle.

An important property of the storage method according to the invention is that several holograms can be stored in the recording material with a laser of fixed frequency in the dimension of the external field. The number of holograms which can be recorded at a fixed wavelength depends on the dielectric strength of the material which limits the possible storage range of the material. The limits of said dielectric strength are entered in Figure 3a, 3b and 3c as A and B and are in the order of magnitude of $\pm 5 \times 10^5$ V/cm. The usable region for the electrical field strength is consequently between A and B. Furthermore, the change in the field strength which results in an extensive disappearance of the absorption change is decisive. From the example of chlorin in a polyvinylbutyral film at the temperature of liquid helium, it is evident that an electrical field strength range of approximately 2×10^4 V/cm is sufficient for storing a hologram. With a film layer thickness of 50 µm, this corresponds to a change of 100 V in the applied voltage. From this it follows that, in the permissible region between A and B, information in the order of magnitude of 50 holograms can be stored for each laser frequency.

As a result of the incidence of light of suitable frequency at the positions of opposite absorption change, the absorption change generated by the narrow-band laser light can be retrieved again.

To read the data, use can be made of the storage device represented in Figure 1. The intensity of the narrow-band laser 1 of fixed frequency is reduced by more than a factor of 100 compared with the write operation. The laser light 8 is incident on the storage material in the electrical field. The transmitted light is a measure of the change in the absorption behaviour achieved in the write operation and is recorded in the detector as a function of the electrical field strength after passing through the optical filter 5 which is intended to suppress interferring light. Figure 3a shows the absorption behaviour of the storage medium before it is exposed to the write process with laser light. Figure 3b shows the absorption behaviour of the sample at a fixed wavelength as a function of the applied electrical field strength after it has been exposed to the laser light at the electrical field strength C. Figure 3c shows the absorption behaviour of the sample at a fixed wavelength as a function of the applied electrical field strength after it has been exposed to the laser light at the electrical field strength C and D. The minima at the positions C in Figure 3b and at the positions C and D in Figure 3c represent the stored items of information. Figure 3d shows the holographic efficiency.

Equipment other than that represented in Figure 1 can also be used for storage and reading. For example, the optical filter may be dispensed with.

The method according to the invention described hitherto operates with a single fixed laser wavelength. The principle presented can also be applied to information storage operations in which the recording material is written on simultaneously or preferably successively, in accordance with the items of information to be stored, at several fixed laser wavelengths which originate from one or more lasers.

Consequently, several discreet laser frequencies (frequency multiplex method) may be combined, for example, with the Stark effect so that, for each laser frequency, a further increase in the information density or a simpler recording of the items of information by means of the voltage can be achieved by additional variation of the Stark voltage.

It is also possible to use several diode lasers (semiconductor lasers) each having a different fixed frequency which record at the same position on the storage medium, each diode being able to record different items of information (a different hologram) at its frequency by variation of the externally applied field, for example, the Stark voltage.

According to the invention, use may also be made of recording materials made of a matrix containing a radiation-sensitive compound according to definition exhibiting at least one inhomogeneously dispersed absorption band, the matrix consisting of a polymer material or a wax which remain solid and chemically stable at room temperature in the interior of electronic equipment, for example up to approx. 60°C without the items of information recorded at lower temperature being erased.

As recording material, it is also possible to employ a polymer matrix in which the radiation-sensitive compound according to definition exhibiting at least one inhomogeneously dispersed absorption band is chemically bound to the polymer matrix or incorporated in the polymer chain, for example anthracene incorporated in polystyrene [cf. Vlauer, P. Remmp, L. Monnerie, Y. Yang, R.S. Stein, Polymer. Communic., 26 (1985), pages 73-76].

Finally, as recording materials, use may also be made of a radiation-sensitive substance according to definition containing matrices in which the molecules of the radiation-sensitive compound are aligned geometrically by suitable preparation techniques. This may be carried out, for example, by adsorption on, or chemical bonding to, a smooth surface or phase boundary, by adsorption on, or bonding to, the surface of small platelets which are introduced in a parallel arrangement into the matrix, coating by the Langmuir-Blodgett technique (described in Chemie in unserer Zeit, No. 9 (1975), pages 173-182) by alignment of the radiation-sensitive compound in an externally applied (for example, electrical) field during the preparation of the storage medium, or by mechanical stretching of the matrix containing the homogeneously distributed radiation-sensitive compound.

Not only a widening of the spectral holes, but also an effective spectral displacement of the band center can be achieved by a parallel alignment of the molecules under the action of an externally applied field, in particular of the Stark effect.

The examples below explain the invention.

Example 1: An optical recording medium (see Figure 2) is prepared by the following method:

0.37 mg of chlorin (7,8-dihydroporphyin, synthesized by the procedure in U. Eisner and R.P. Linsteadt, Journal of the Chemical Society 4 (1955), pages 3742-3749) are dissolved in 2 ml of methylene chloride (Merck, UVASOL). 600 mg of polyvinylbutyral with a molecular weight of 38,000-45,000 (Polyscience Inc., Warrington, Pennsylvania 18978, USA) are dissolved in 10 ml of methylene chloride (Merck, UVASOL). The two solutions are thoroughly mixed in a crystallizing dish with a diameter of 4 cm and then allowed to stand at room temperature until the solvent has evaporated. A rectangular piece with a size of 1 x 2 cm is cut out of the middle of the coloured plastic plate approx. 0.2 mm thick left behind on the bottom of the dish and mounted in the following manner:

2 glass plates (10 x 24 x 1 mm) [(9), Figure 2] on which an electrically conducting, optically transparent tin dioxide film has been vapour deposited on one side, are joined together with a lateral offset of approx. 5 mm to form a sandwich stack so that the plastic material is in the centre and is in contact on both sides with an electrode. The entire sandwich is then cemented under pressure at 100°C

for 12 hours, the thickness of the plastic material film being adjusted to 0.2 mm by feeler gauges in the press.

Contact is made to the two electrodes [(4), Figure 2] with wires [(7), Figure 2] and then the entire sandwich is mounted on an insulating carrier.

For the optical recording and reproduction, an apparatus with the following main components is used (see Figure 4):

- A bath-type cryostat (11) for liquid helium with two pairs of windows arranged parallel to each other and a vacuum connection for working with reduced helium pressure;
- A dye laser (1a) excited by an argon-ion laser (1) at 488 nm with a tuning unit and frequency stabilization (line width about 1 MHz, Model CR-599-21 manufactured by Coherent, Palo Alto, CA. 94304, USA) provided with the laser dye DCM manufactured by Exciton, Overlook Station, Dayton, OH 45431, USA;
- Detection equipment consisting of a residual light amplifier (16) and a commercial video camera (17) with monitor and video recorder (not shown);

To record a hologram, a holder with the recording material is incorporated in the cryostat (11) so that it is positioned between the windows; the cryostat is sealed so as to be vacuum tight and cooled down to about 4 K by filling with liquid helium. The temperature is then reduced by a further 2 K by pumping off gaseous helium at 1000 Pa.

The output ray of the dye laser (1a) is adjusted to 635 nm and stabilized, attenuated to a power of 1 µW, then expanded with a beam telescope (12) having a magnification factor of 15 and split into two partial rays of equal power (termed the object ray (14) and the reference ray (15)) with a tube-shaped ray divider (13). The two partial rays are directed approximately perpendicularly to the recording platelet (10) in the cryostat (11) by deflection with adjustable mirrors (S_2, S_3, S_4) so that they intersect on it at an angle of 10°. The total beam can be interrupted by means of a first electrically operated flap (18) between the telescope (12) and the ray divider (13) and the object ray (14) by a further flap (19) downstream of the ray divider. To record a first hologram, a voltage of -500 V coming from a voltage-source (21) is applied to the electrodes (20) of the recording platelet (10) with the laser beam interrupted, a first image (a diapositive with a black/white line drawing (22)) is placed in the object ray and then the two laser rays are released by opening the flaps (4) and (8) for 20 seconds. The voltage is then increased by 200 V to -300 V, a second image is placed in the object ray and again illuminated for 20 seconds. This operation is repeated furthermore at -100 V, +100 V and +300 V.

To reproduce the individual images, the laser is attenuated to approx. 0.1 µW at the same wavelength, but only the reference ray (15) is released. The latter is now diffracted at the recording platelet (10) and may be imaged via a lens (23) with a focal length of 25 cm on the residual light amplifier (16). At the focus behind the lens, interferring stray light is blocked off by a pinhole diaphragm (24) with a diameter of 1 mm. The 5 images recorded are reproduced, if desired separately, via the video camera (17) by applying the voltages between -500 V and +300 V used during recording.

In the present Example 1 (chlorin in polyvinylbutyral film), the incidence of light in the wavelength spectral region of 625-640 nm results in the process of photochemical hole burning. In this process, the chlorin molecule undergoes a photoreactive under the influence of light, the new photoproduct generated absorbing in the region of 560-580 nm. This protection is reversible, and the stored information can be erased with high efficiency by the incidence of ight in the spectral region of 560-580 nm or even in a wider absorption band of the photoproduct. A complete erasure of the stored information also occurs if the storage medium is heated up to room temperature.

Example 2: Procedure and apparatus are analogous to Example 1, but instead of chlorin, a solution containing 0.35 mg of 4-oxazine perchlorate (laser grade, manufactured by Eastman Kodak, Rochester, NY 14692) in 2 ml of methylene chloride is used for the preparation of the recording material. The dye laser is in this case adjusted to 620 nm for the recording and reproduction.

Example 3: Procedure and apparatus are analogous to Example 1, but instead of chlorin, a solution containing 0.35 mg of cresyl violet (laser grade, manufactured by Eastman Kodak, Rochester, NY 14692) in 2 ml of methylene chloride is used for the preparation of the recording material. The dye laser is in this case adjusted to 625 nm for the recording and reproduction.

Example 4: A recording material is prepared according to Example 1, but instead of chlorin, 0.5 mg of phthalocyanine (Fluka, Switzerland) is used. Hole burning is performed at a laser wavelength of 690 nm, the image in the sample beam is replaced with a simple aperture, and the total signal intensity is detected with a photomultiplier.

Example 5: A pellet of 0.5 g of low density linear polyethylene is placed in a flat dish on a hot plate at 150°C to heat it above the glass transition point. A dye solution prepared from 0.35 mg chlorin (prepared according to Example 1) and 2 ml dichloromethane is added dropwise. The polyethylene is kneaded with a spatula to disperse the dye homogeneously in the soft pellet. The polymer is spread out to a flat disc of 0.5 mm thickness with the spatula, while it is still hot, and then quenched to room temperature. A piece is cut from this disc and placed between two conducting glass plates, following the procedure of Example 1. Hole burning is performed according to Example 1 at a laser wavelength of 635 nm, and the image in the sample beam is replaced with a simple aperture.

Example 6: A pellet of 0.5 g of polystyrene (type 144C013, BASF) is placed in a flat dish on a hot plate at 190°C to heat it above the glass transition point. A dye solution prepared from 0.35 mg chlorin (prepared according to Example 1) and 2 ml dichloromethane is added dropwise. Simultaneously, the polystyrene is kneaded with a spatula to disperse the dye homogeneously in the soft pellet. Then the polymer is spread out to a flat disc of 0.5 mm thickness with the spatula, while it is still hot, and finally cooled to room temperature. A piece is cut from this disc and placed between two conducting glass plates, following the procedure of Example 1. Hole burning is performed according to Example 1 at a laser wavelength of 635 nm, and the image in the sample beam is replaced with a simple aperture, and the total signal intensity is detected with a photomultiplier.

Example 7: A silica glass sample is prepared by the sol-gel procedure from a solution of 0.6 mg oxazine-4-perchlorate (Kodak, Rochester, NY 14692), dissolved in 10 ml tetraethoxy silane (Fluka, Switzerland), 3.7 ml distilled water, 11.4 ml ethanol and 0.1 ml hydrochloric acid (1 molar). 2.5 ml of this solution are poured into a cylindrical glass dish of 2 cm diameter, then a large beaker is used as a bell jar to enclose the small cylinder. The solvents are allowed to evaporate very slowly at room temperature, whereby the mixture solidifies within four weeks. The solid pellet is removed from the glass and kept at room temperature for another two months. The finished pellet can be ground and polished to optical standards and is then placed in the cryostat. Hole burning is performed as in Example 5, but no electrodes are attached to the sample, and so only an exposure and reading at zero volt is possible, and the laser is tuned to 620 nm.

Example 8: Recording medium, apparatus and procedure are as described in Example 2, but two independent series of five images are recorded, one at a laser wavelength of 619 nm, for the other the laser is tuned by 0.02 nm to higher wavelength. Thus, a total of ten different pictures are stored in one exposure position. Readout of any of the ten stored images is performed at the corresponding recording wavelength and Stark voltage.

Patent claims

1. A method of optically recording and reading items of information in a recording material which contains at least one radiation-sensitive compound having at least one inhomogeneously dispersed absorption band in the UV and/or visible and/or IR spectral region, which compound, under the action of narrow-band laser light with at least one frequency lying within said absorption band and under the action of an externally adjustable electrostatic, magnetic or pressure field, undergoes a change in the absorption behaviour, such that, by adjustment to another field strength of the electrostatic, magnetic or pressure field, further changes in the absorption behaviour can be produced and therefore additional items of information recorded, which changes, however, can be read off again on reproducing the field strengths at the time of recording, wherein the items of information are recorded and read in the form of holograms.

2. A method according to claim 1, wherein an electrostatic field is employed as externally adjustable field.

3. A method according to claim 1, wherein the recording material is high-molecular weight organic material of natural or synthetic orgigin, glass, ceramic glass or a frozen liquid.

4. A method according to claim 3, wherein the recording material is an amorphous transparent material.

5. A method according to claim 3, wherein the high-molecular weight organic material is a polyacrylate, a polycyanoacrylate, polyethylene, polypropylene, polystyrene, a polyvinylacetal, polyvinylcarbazole or a polyvinyl alcohol.

6. A method according to claim 1, wherein the radiation-sensitive compound undergoes a change in the absorption profile of the inhomogeneously dispersed band affected by the laser frequency as a result of the process of photophysical or photochemical hole burning.

7. A method according to claim 1, wherein the radiation-

sensitive compound absorbs in the UV and/or visible and/or near IR spectral region.

8. A method according to claim 7, wherein the radiation-sensitive compound absorbs in the visible and/or near IR spectral range.

9. A method according to claim 6, wherein the radiation-sensitive compound is a porphin derivative, a porphyrazine, quinazarine, an α-diketone, an oxazine, a tetrazine, a spiropyran, an isoimidazole, an azirin, and also a laser dye.

10. A method according to claim 1, wherein the radiation-sensitive compound is present in a quantity of 0.001 to 30% by weight referred to the recording material (matrix).

11. A method according to claim 1, wherein the recording material is present in the form of a film to which an electrical field can be applied by two electrodes.

12. A method according to claim 11, wherein the film is arranged between two transparent glass plates which each carry an electrode for generating the electrical field.

13. A method according to claim 1, wherein the recording material is written on, in accordance with the items of information to be stored, in each case at a fixed laser frequency with an externally applied field which changes stepwise, each recording and reading operation being carried out in each case at a field strength which remains constant.

14. A method according to claim 1, wherein the absorption change produced by narrow-band laser light can be retrieved again by the incidence of light of suitable frequency at the positions of opposite absorption change.

15. A method according to claim 1, wherein the recording material is written on simultaneously or successively, in accordance with the items of information to be stored, at several fixed laser wavelengths which originate from one or more lasers.

16. A method according to claim 15, wherein the recording material is written on successively.

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