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[GB/GB]; 1 Mount Pleasant, Stow On The Wold, Gloucestershire GL54 1AL (GB). **OSWALD, Iain** [GB/GB]; 11 Roseneath Terrace, Edinburgh EH9 1JS (GB).

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(74) Agent: **RUSHTON, D., J.**; Ip QinetiQ Formalities, Cody Technology Park, A4 Building Ively Road, Farnborough, Hampshire GU14 0LX (GB).

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(71) Applicant (*for all designated States except US*): **QINETIQ LIMITED** [GB/GB]; 85 Buckingham Gate, London SW1 6TD (GB).

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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **SAGE, Ian, Charles** [GB/GB]; Qinetiq Malvern, St Andrews Road, Malvern, Worcs WR14 3PS (GB). **BOURHILL, Grant, Hannah**

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**WO 03/016429 A1**

(54) Title: TRIBOLUMINESCENT MATERIALS AND DEVICES

(57) Abstract: This invention relates to various phosphine oxides and their use in applications which exploit the triboluminescent effect.

### **Triboluminescent Materials and Devices**

This invention relates to novel Triboluminescent (TL) materials and their use in devices which exploit the triboluminescent effect.

Triboluminescent materials are known – (L M Sweeting & J L Guido, J. of Luminescence, 33, (1985), p167, N Kitamura et al, Chem Phys Letts, 125, (1986), p360, B P Shandra, et al Pramana-J Phys, 29, (1987), p399, C R Hurt, et al Nature, 212, (1966), p179; L M Sweeting & A L Rheingold, J Am Chem Soc, 109,(1987), p2652 M B Hocking, et al, J. of Luminescence, 43, (1989), p309). Chinese Chemical Letters, vol 11, no 7 pp635-38, 2000 discloses a number of compounds that exhibit mechanoluminescence (ML). The property of mechanoluminescence is effectively the same property as triboluminescence. More specifically two 1:1 binuclear (europium and lanthanum)  $\beta$ -diketonate complexes are disclosed. The complexes further comprise 1,10-phenanthroline and an anion of thenoyltrifluoroacetone (HTTA). Soden in J. Appl. Phys., 32, (1961) 750 discloses the effects of rare-earth substitutions on the fluorescence of Terbium Hexa-Antipyrine tri-iodide.

Triboluminescence is the effect seen when a material emits light when particles of the material are damaged/fractured or strained.

PCT GB96/02778 and corresponding US 5905260 describe the use of triboluminescent compounds in an environment where they are used to detect damage to objects.

The following references disclose a number of fluorescent materials:

EP 0744451, EP 0556005, US 5658494, US 3551345, PCT/GB98/01773, chemical abstracts 128:148933, 103:226494, 101:45857.

Preferably for use in damage sensing equipment triboluminescent compounds exhibit some or all of the following properties:

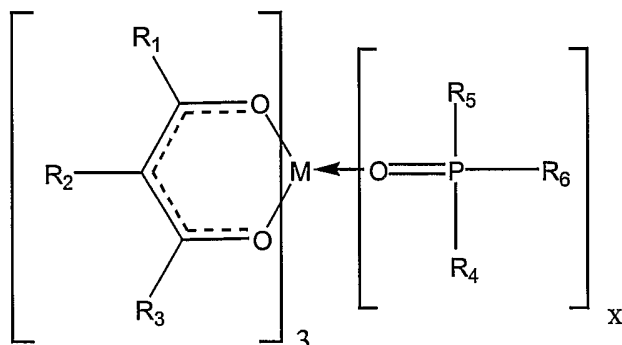
- Bright emission
- High stability to temperature and high melting point
- Compatibility with structural and adhesive resins
- Emission at wavelengths which are different from those provided by known materials
- Emission of light having other features distinguishable from known materials, such as luminescence lifetime, bandwidth etc.

Clearly it is also advantageous that triboluminescent compounds, if they are to be used commercially, are not prohibitively expensive.

There is a continued need for triboluminescent materials for use in such an environment and it is an object of the present invention *inter alia* to provide alternative compounds suitable for use in a range of applications/devices which are capable of exploiting the triboluminescence effect particularly sensing damage applications.

The current invention provides for, *inter alia*, the use of a range of compounds in a number of devices/applications which exploit the triboluminescent effect.

According to a first aspect of the present invention materials of formula I are provided:



Formula I

wherein

x is 1 or 2

M is selected from Europium, Terbium, Dysprosium and Samarium;

R1, R2 and R3 are independently of each other selected from phenyl, naphthyl, H and C1-C6 branched or straight chain alkyl, thiophene and C1-C6 fluorinated alkyl wherein the fluorination may be in 1 or all positions or any intermediate value, substituted phenyl wherein the substituents are independently selected from C1-C4 straight or branched chain alkyl, Cl, Br, F, I and the phenyl group may be substituted in 1, 2 or 3 positions;

R4 and R5 are independently of each other selected from phenyl, tolyl, naphthyl, C1-C6 branched or straight chain alkyl and substituted phenyl wherein the substituents are independently selected from C1-C4 straight or branched chain alkyl and the phenyl group may be substituted in 1, 2 or 3 positions;

R6 is selected from phenyl, tolyl, naphthyl, C1-C6 branched or straight chain alkyl,  $-(CH_2)_nP(O)R_7R_8$ , wherein  $n=1$  to 4 and  $-N=(P R_7 R_8 R_9)$ , wherein R7, R8 and R9 are independently selected from phenyl, naphthyl, C1-C6 branched or straight chain alkyl and substituted phenyl wherein the substituents are independently selected from C1-C4 straight or branched chain alkyl and the phenyl group may be substituted in 1, 2 or 3 positions;

R6 is also selected from substituted phenyl wherein the substituents are independently selected from C1-C4 straight or branched chain alkyl and the phenyl group may be substituted in 1, 2 or 3 positions;

It is understood in the definition of R6 that the phosphine oxide group, [included in  $-(\text{CH}_2)_n\text{P}(\text{O})\text{R}_7\text{R}_8$ ] if present, may be coordinated to the metal atom M or to another equivalent metal atom as a bridging group.

Preferably

R1, R2 and R3 are independently of each other selected from phenyl, and C1-C4 branched or straight chain alkyl,

R4 and R5 are independently of each other selected from phenyl, tolyl and C1-C6 branched or straight chain alkyl,

R6 is selected from phenyl, tolyl, C1-C6 branched or straight chain alkyl, and 2-diphenylphosphinoxyethyl.

According to a second aspect of this invention a method of making paper that emits light when torn and/or pressed and/or gripped and/or folded comprises the steps of coating and/or impregnating the paper with triboluminescent material according to the first aspect of the present invention.

When coating and/or impregnating the paper it may be necessary to apply the triboluminescent material in one or more of a number of ways, for example:

- in an adhesive composition, in addition the triboluminescent material may be glued onto the paper either directly and/or in an encapsulant such as a polymer;
- in a solvent followed by solvent evaporation;
- by melting the triboluminescent material such that it soaks into the paper;
- by incorporating the triboluminescent material together with the pulp, fibre etc., during manufacture of the paper.

Preferably the solvent will be an organic solvent though this will be a function of the solvation properties of the triboluminescent material.

Examples of suitable polymers for use in encapsulation include the following:

Acrylic and methacrylic resins, polyimides, polyamides, melamine/formaldehyde resins, urea formaldehyde resins, epoxy resins, poly(p-xylylene), gelatin, poly(lactic acid), polyester resins and alkyd resins.

Typical adhesives include:

Epoxy adhesives based on adducts of bisphenol-A and epichlorhydrin cured by polyamine or anhydride initiators, and similar adhesives based on other epoxides, UV curable and thermally curable adhesives based on acrylic, vinylic, styrenic, or thiol/ene monomer systems, cyanoacrylate adhesives, pressure sensitive adhesives, hot melt adhesives, latex based adhesives, PVA adhesives, solvent based adhesives, urea formaldehyde and melamine formaldehyde adhesives, anaerobic adhesives, bis-diallylamine derived adhesives etc.

In addition to the adhesive and triboluminescent material the adhesive composition may also comprise one or more of the following additional reagents such as solvents, dispersants, plasticisers, curing agents, dyes, fillers, stabilisers, anti-oxidants etc as is understood in the art. The compositions may include water as a solvent or dispersant or an organic solvent such as dichloromethane, acetone, tetrahydrofuran etc. may be present in order to ensure that the composition is homogenous and will spread well.

According to a third aspect of this invention paper is provided which comprises one or more triboluminescent materials according to the first aspect of the present invention such that the paper triboluminesces when the paper is torn and/or pressed and/or gripped and/or folded.

Such paper is obtainable by the method of the second aspect of the invention.

For all of the above aspects of the invention the term paper is also taken to include paper-like products such as cardboard, kitchen-roll, tissue and the like.

According to a fourth aspect of the invention a product comprising the paper of the third aspect of the invention is provided.

According to a fifth aspect of this invention an adhesive composition comprising an adhesive and one or more triboluminescent materials according to the first aspect of the present invention is provided.

According to a sixth aspect of this invention a method of adhering two surfaces together comprises the steps of:

applying an adhesive composition to one or more surfaces and bringing the surfaces into contact such that adhesion occurs wherein the adhesive composition comprises an adhesive and one or more triboluminescent materials according to the first aspect of the present invention.

According to a seventh aspect of this invention a method of making adhesive tape that flashes when used comprises the steps of:

selecting a substantially transparent substrate,  
optionally depositing an adhesion promoter on the substrate,  
depositing an adhesive composition comprising a triboluminescent material according to the first aspect of the present invention on to the substrate,  
optionally drying the adhesive composition,  
optionally depositing a further laminating sheet on top of the adhesive composition before or after any drying stage.

The laminating sheet, if applied, may be treated with a release layer.

By flashes when used it is meant that the adhesive tape may flash when it is removed from a roll of adhesive tape or it may flash when it is removed from the object to which it has been applied. The adhesive tape may also flash when it is cut. How many times a particular piece of adhesive tape flashes will depend on the nature of the triboluminescent materials used and the adhesive and the substrate to which it has been adhered.

Drying may be carried out using any of the known techniques – these include:

Solvent removal, removal of a dispersant phase, chemical polymerisation or cross linking, chemical reaction or condensation and may be aided by known methods such as application of heat or UV light.

The substrate may comprise triboluminescent material itself, typically this would be carried out during formation of the substrate.



There are various uses to which the adhesive compositions and methods of the present invention may be put. Included are adhesive compositions when used on envelopes and tape and the like for indicating whether or not an envelope or package has been previously opened. Alternatively, seals on containers may comprise adhesive/triboluminescent compositions according to the present invention so it is evident whether or not a container has been tampered with or damaged such that the seal has been broken in some way. For some of these particular type applications the adhesive and triboluminescent materials may with advantage be selected such that the composition only triboluminesces once.

Hence an eighth aspect of this invention provides a method for detecting tampering of a sealed article comprising the steps of:

coating a part of an unsealed article with an adhesive composition,  
sealing the article,

wherein the adhesive composition further comprises one or more triboluminescent materials according to the first aspect of the present invention such that on breaking the seal triboluminescence will be observed.

The article may be any type of suitable container, for example an envelope or packaging or a bottle and top.

In the above method it is also possible for the adhesive/triboluminescent mixture to be applied once the article has been sealed in some way. An example of this could be a bottle with a screw top wherein the adhesive/triboluminescent mixture could be added once the top has been screwed on to the bottle. The mixture could also be added before and after the sealing.

The present invention also provides for opening packages, envelopes and the like with added aesthetic appeal. It is an objective of the present invention to provide aesthetic effects in relation to adhesives/adhesive tape/paper, paper-like products through the use of technical structures and/or other technical means.

Further aspects of the invention include articles produced by the above methods.

Typical adhesives include:

Epoxy adhesives based on adducts of bisphenol-A and epichlorhydrin cured by polyamine or anhydride initiators, and similar adhesives based on other epoxides, UV curable and thermally curable adhesives based on acrylic, vinylic, styrenic, or thiol/ene monomer systems, cyanoacrylate adhesives, pressure sensitive adhesives, hot melt adhesives, latex based adhesives, PVA adhesives, solvent based adhesives, urea formaldehyde and melamine formaldehyde adhesives, anaerobic adhesives, bis-diallylamine derived adhesives etc..

In addition to the adhesive and triboluminescent material the adhesive composition may also comprise one or more of the following additional components such as solvents, wetting agents, flow modifiers, plasticisers, curing agents, dyes, fillers, stabilisers, anti-oxidants etc as is understood in the art. The compositions may include water as a solvent or dispersant or an organic solvent such as dichloromethane, acetone, tetrahydrofuran etc. may be present in order to ensure that the composition is homogenous and will spread well.

According to a ninth aspect of this invention a damage-sensing device comprises at least one light sensor and at least one triboluminescent material according to the first aspect of the current invention.

The light sensor may be connected directly to the triboluminescent material or via light guiding means such as optical fibres.

The sensor may be embedded within a structure, such as a composite plastics material, or fixed externally to such a structure. Several sensors may be embedded within one structure. Light output from the triboluminescent material may be detected directly, or such light output may be absorbed by photo excitable dye material whose subsequent luminescence is detected. Different triboluminescent material described by the present invention and or different dyes may be used in different parts of a structure so that damage location is readily determined from the wavelength of emission. The detector may be directly connected to each different triboluminescent or dye material, or one or more detectors used with filters or wavelength detection means to determine the location of damage at several sites.

Additionally the damage site may be located by timing receipt of pulses. The intensity of emission may also be measured to give an indication of the severity of impact and hence damage.

The light guiding means may be single or multimode optical fibres, optical transparent sheet or slab within a composite material. The sheet material may have waveguides defined by rib, indiffusion, or etching etc, and may contain secondary emitters.

The detectors may be photo multipliers, photo diodes, as single detectors or in arrays.

Use of the materials of the present invention may be incorporated into the devices described in US 5905260 the contents of which are incorporated herein by reference.

The invention will now be described, by way of example only, with reference to the accompanying drawings of which:-

Figure 1 is a sectional view of a sensor embedded within a structure;

Figure 2 is similar to and a variation of Figure 1;

Figure 3 is a sectional view of two sensors embedded within a structure, with optical fibre readout to a single detector;

Figure 4 is a sectional view of a sensor mounted on a surface of a structure;

Figure 5 is a sectional view of several triboluminescent materials and a light guiding layer embedded within a structure;

Figure 6 is similar to that of Figure 5, but in addition has a different photo excitable dye associated with each triboluminescent material;

Figure 7 is a perspective view of a sensor employing three differently doped fibres each directing light from several triboluminescent materials to a single detector.

As seen in Figure 1 a sensor 1 is embedded in a composite material 2 such as a glass or carbon fibre matrix layered material. The sensor 1 comprises a small crystal 3 of a triboluminescent (TL) material as described by the present invention held within a cavity 4 by epoxy resin 5 and optically connected by optical cement such as a UV curing glue 6 from the Norland [TM] range to an optical fibre 7 which transmits light to an externally mounted detector 8. This detector 8 may be a photo diode or part of an array linked to several crystals.

The composite material 2, may have different triboluminescent materials 3 with their characteristic emissions arranged at different positions within the composite 2. The detectors 8 detect such different wavelengths thereby giving positional information about damage location

In operation, e.g. in an aircraft, impact of objects on the composite 2 above a predetermined known energy level will damage the crystal 3 causing it to emit light; high impact energy results in higher light output. The detected light may either be transmitted as a signal directly to the pilot if a serious damage had occurred or stored by computer and read by a maintenance crew at a later stage for damage repair. If the recorded detection indicates composite damage, then that part of the composite may be repaired or replaced before the next aircraft flight.

Thus several different materials constructed as in Figure 1 may be used as shown in different parts of a structure and a single detector used. In this case the detector must be able to distinguish different wavelengths to indicate which area of the structure has received damage.

Figure 2 is similar to Figure 1 and given like reference numeral. In this example the optical fibre 7 optically connects to glue 5 holding the crystal 3 within the cavity 4. The glue 5 is optically transparent and may be a polymer matrix.

Figure 3 shows different TL crystals 10, 11 (two only shown, but may be many more) located in cavities 12, 13 in different parts of a composite material 14. A single detector 15 connects with each crystal 10, 11 via an optical fibre network 16 and is sensitive to the different emissions of the crystals 10, 11, and can therefore indicate the location of any damage. Such an arrangement reduces the number of cavities needed within the composite material 14.

Figure 4 shows how a sensor 20 can be mounted externally on a composite material 21. As before one or more TL crystals 22 are encapsulated within an optically transparent glue or resin 23 and coupled to a detector 24 via an optical fibre 25. When a plurality of different crystals 22 are used, the detector 24 is arranged to distinguish between their different emissions wavelengths to give an indication of damage location. A protective layer 26 of opaque material covers the glue 23.

Figure 5 shows a composite material 30 in which a layer 31 of a guiding material is sandwiched between two layers 32, 33. Embedded within the light guiding layer 31 are one or more TL crystals 34. A detector 35 is mounted on the edge of the

composite material 30. Suitable materials for the light guiding layer 31 include:- UV curing glues, sol-gel, optically transparent polymers, resins or glues.

Figure 6 shows a composite material 40 in which a layer 41 of a light guiding material is sandwiched between two layers 42, 43. Embedded within the layer 41 are three TL crystals 44, 45, 46. Above each crystal 44, 45, 46 is a volume of three different photo excitable dyes 47, 48, 49 contained within a second layer 50 of a light guiding material. A detector 51 is sensitive to the outputs of each dye volume 47, 48, 49. When damage occurs, an appropriate crystal 44, 45, 46 will emit light and cause an associated dye volume 47, 48, 49 respectively to emit light at a characteristic wavelength which is guided by the layer 50 to the detector 51.

Figure 7 shows a composite layer material 60 in which several TL crystals 61, 62, 63 are embedded in rows within a layer 64. Optical fibres 66, 67, 68 containing photo excitable dyes are in optical contact with these rows of crystals 61, 62, 63 and connect via an optical fibre network 69 to one or more detectors 70. The fibres 66, 67, 68 are embedded in an optically transparent layer 71 and covered with a protective layer 72 of composite fibre. The crystals 61, 62, 63 may be one of the adducts of the present invention, the fibres 66, 67, 68 maybe glass single or multi mode fibres, or polymer fibres; the glues may be RS [TM] bipax epoxy, Araldite [TM] fast setting, or Norland UV curing flues.

In a modification of Figure 7 an additional set of differently doped optical fibres is arranged in columns so that an x,y matrix of differently doped optical fibres lies within a composite material. The column fibres are connected to one or more detectors as in Figure 7. Signals from these two detectors indicate where in the matrix, light is being received.

A flashing form of paper, (e.g. writing paper, tissue or cardboard) according to the present invention may be fabricated as follows. Paper is soaked in a solution of triboluminescent material and any excess solvent is evaporated off. The paper may then be torn, folded or crumpled to test for a triboluminescent effect.

An alternative method of fabrication involves melting the triboluminescent material and allowing the melt to soak into the paper.

An alternative method of fabrication involves gluing triboluminescent material to the surface of the paper, alternatively the triboluminescent material is encapsulated, for example, in polymer which may then be coated on to the surface of the paper. Examples of suitable polymer include poly vinyl alcohol. The polymer may be applied whilst still in monomer form and subsequently cured.



A flashing form of adhesive tape according to the present invention may be fabricated as follows. An adhesive compound which may be cured via any of the known methods of curing including by uv polymerisation and a triboluminescent material are placed on to a sheet of plastic material. A further sheet of plastic is pressed on top of the first sheet, sandwiching the adhesive/triboluminescent mixture. The sheets plus mixture are then subject to curing such that the monomer polymerises – it may be the case that an amount of the monomer remains unpolymerised. In order to assess the tape the sheets may be pulled apart to reveal bright flashes.

It is not necessarily the case that the adhesive is a monomer system – any type of adhesive known to those skilled in the art would be suitable. The mixture need not necessarily require curing.

Example triboluminescent complexes according to the invention were prepared by the methods described below. In assessing the relative brightnesses of triboluminescent materials, it is understood by those skilled in the art that quantitative comparisons are made difficult by the dependency of the triboluminescent emission intensity on such factors as the crystalline particle size and crystal habit of the sample, the force applied to the sample, traces of different impurities which may occur in the sample, the geometry of the optical detector and its wavelength sensitivity. For the purpose of evaluating the usefulness of the compounds of the invention, a semi-quantitative scale was employed based on observation of the triboluminescent emission from the samples by eye, while the materials in the form of crystalline powders were crushed in a soda lime glass sample tube under hand pressure with a stainless steel spatula. The brightness is then assessed according to the highest level of ambient illumination, in the presence of which the triboluminescent emission becomes visible. The scale employed is:

<b>Brightness Scale</b>	<b>Maximum ambient light for observation</b>
10	Full daylight
9	Diffuse daylight
8	Bright room lighting
7	Subdued room lighting
6	Dim artificial light
5	Semi-darkness
4	Darkness, without dark adaptation of the eye
3	Darkness, with up to 2 mins dark adaptation
2	Darkness, with up to 10 mins dark adaptation
1	Visible with fully dark adapted eye
0	No observable triboluminescence

Compounds of this invention may be prepared by means which are apparent to those skilled in the art. Known metal tris  $\beta$ -diketonates may be reacted with one or two molar quantities of substituted phosphine oxides. Phosphine oxides are known materials which are in many cases commercially available. In cases where the phosphine oxide is not a commercial product, but the phosphine is available, the phosphine may be oxidised to the phosphine oxide, for example by treatment with an excess of hydrogen peroxide in ethanol. An alternative synthesis comprises the combination of the  $\beta$ -diketone, the phosphine oxide and a salt of the metal in appropriate molar ratios with a small excess of a base. A suitable base includes potassium ethoxide, when the reaction is conveniently carried out in solution in ethanol. Preferably the reagents and solvents used in the synthesis, irrespective of the route chosen, are substantially anhydrous. Purification of the products may be carried out by recrystallisation from a solvent eg., from anhydrous ethanol or dry toluene.

Example synthesis: Tris 2,2,6,6-tetramethylheptanedionato terbium triphenylphosphine oxide adduct

Terbium tris 2,2,6,6-tetramethylheptanedionate (1g) and triphenylphosphine oxide (0.393g) were added to anhydrous ethanol (3ml). The mixture was warmed to dissolve the solid, and then raised to boiling for 10 minutes. The solution was cooled to room temperature and then to 0°C to induce crystallisation of the product. The off-white solid was filtered off and recrystallised from anhydrous ethanol and dried in vacuo at 60°C to yield tris 2,2,6,6-tetramethylheptanedionato terbium triphenylphosphine oxide adduct (0.9g) as a white solid.

The following compounds were synthesised in the same way:

Tris acetylacetonato terbium triphenylphosphine oxide adduct

Tris acetylacetonato terbium tritolylphosphine oxide adduct

Tris acetylacetonato terbium 1-naphthylidiphenylphosphine oxide adduct

Tris acetylacetonato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris acetylacetonato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris acetylacetonato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris acetylacetonato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris dibenzoylmethanato terbium triphenylphosphine oxide adduct

Tris dibenzoylmethanato terbium tritolylphosphine oxide adduct

Tris dibenzoylmethanato terbium 1-naphthyldiphenylphosphine oxide adduct

Tris dibenzoylmethanato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris dibenzoylmethanato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris dibenzoylmethanato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris dibenzoylmethanato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris thenoyltrifluoroacetonato terbium triphenylphosphine oxide adduct

Tris thenoyltrifluoroacetonato terbium tritolylphosphine oxide adduct

Tris thenoyltrifluoroacetonato terbium 1-naphthyldiphenylphosphine oxide adduct

Tris thenoyltrifluoroacetonato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris thenoyltrifluoroacetonato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris thenoyltrifluoroacetonato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris thenoyltrifluoroacetonato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato terbium triphenylphosphine oxide adduct  
brightness=4

Tris 2,2,6,6-tetramethylheptanedionato terbium tritolylphosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato terbium 1-naphthyldiphenylphosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 3-methylpentane-2,4-dionato terbium triphenylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato terbium tritolylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato terbium 1-naphthyldiphenylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato terbium triphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato terbium tritolylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato terbium 1-naphthyldiphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris pivaloyltrifluoroacetato terbium triphenylphosphine oxide adduct

Tris pivaloyltrifluoroacetato terbium tritolylphosphine oxide adduct

Tris pivaloyltrifluoroacetato terbium 1-naphthyldiphenylphosphine oxide adduct

Tris pivaloyltrifluoroacetato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris pivaloyltrifluoroacetato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris pivaloyltrifluoroacetato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris pivaloyltrifluoroacetato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris trifluoroacetylacetonato terbium triphenylphosphine oxide adduct

Tris trifluoroacetylacetonato terbium tritolylphosphine oxide adduct

Tris trifluoroacetylacetonato terbium 1-naphthyldiphenylphosphine oxide adduct

Tris trifluoroacetylacetonato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris trifluoroacetylacetonato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris trifluoroacetylacetonato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris trifluoroacetylacetonato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris hexafluoroacetylacetonato terbium triphenylphosphine oxide adduct

Tris hexafluoroacetylacetonato terbium tritolylphosphine oxide adduct

Tris hexafluoroacetylacetonato terbium 1-naphthylidiphenylphosphine oxide adduct

Tris hexafluoroacetylacetonato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris hexafluoroacetylacetonato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris hexafluoroacetylacetonato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris hexafluoroacetylacetonato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato terbium triphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato terbium tritolylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato terbium 1-naphthylidiphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato terbium triphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato terbium tritolylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato terbium 1-naphthylidiphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato terbium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato terbium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato terbium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato terbium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris acetylacetonato europium triphenylphosphine oxide adduct

Tris acetylacetonato europium tritolylphosphine oxide adduct

Tris acetylacetonato europium 1-naphthyldiphenylphosphine oxide adduct

Tris acetylacetonato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris acetylacetonato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris acetylacetonato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris acetylacetonato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris dibenzoylmethanato europium triphenylphosphine oxide adduct

Tris dibenzoylmethanato europium tritolylphosphine oxide adduct

Tris dibenzoylmethanato europium 1-naphthyldiphenylphosphine oxide adduct

Tris dibenzoylmethanato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris dibenzoylmethanato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris dibenzoylmethanato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris dibenzoylmethanato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris thenoyltrifluoroacetonato europium triphenylphosphine oxide adduct

Tris thenoyltrifluoroacetonato europium tritolylphosphine oxide adduct

Tris thenoyltrifluoroacetonato europium 1-naphthyldiphenylphosphine oxide adduct

Tris thenoyltrifluoroacetonato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris thenoyltrifluoroacetonato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris thenoyltrifluoroacetonato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris thenoyltrifluoroacetonato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato europium triphenylphosphine oxide adduct  
brightness=3

Tris 2,2,6,6-tetramethylheptanedionato europium tritolylphosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato europium 1-naphthyldiphenylphosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 3-methylpentane-2,4-dionato europium triphenylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato europium tritolylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato europium 1-naphthyldiphenylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato europium triphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato europium tritolylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato europium 1-naphthyldiphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris pivaloyltrifluoroacetato europium triphenylphosphine oxide adduct



Tris pivaloyltrifluoroacetato europium tritolylphosphine oxide adduct  
Tris pivaloyltrifluoroacetato europium 1-naphthylidiphenylphosphine oxide adduct  
Tris pivaloyltrifluoroacetato europium bisdiphenylphosphinoethane bis P-oxide adduct  
Tris pivaloyltrifluoroacetato europium bisdiphenylphosphinopropane bis P-oxide adduct  
Tris pivaloyltrifluoroacetato europium bisdiphenylphosphinobutane bis P-oxide adduct  
Tris pivaloyltrifluoroacetato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct  
Tris trifluoroacetylacetonato europium triphenylphosphine oxide adduct  
Tris trifluoroacetylacetonato europium tritolylphosphine oxide adduct  
Tris trifluoroacetylacetonato europium 1-naphthylidiphenylphosphine oxide adduct  
Tris trifluoroacetylacetonato europium bisdiphenylphosphinoethane bis P-oxide adduct  
Tris trifluoroacetylacetonato europium bisdiphenylphosphinopropane bis P-oxide adduct  
Tris trifluoroacetylacetonato europium bisdiphenylphosphinobutane bis P-oxide adduct  
Tris trifluoroacetylacetonato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct  
Tris hexafluoroacetylacetonato europium triphenylphosphine oxide adduct  
Tris hexafluoroacetylacetonato europium tritolylphosphine oxide adduct  
Tris hexafluoroacetylacetonato europium 1-naphthylidiphenylphosphine oxide adduct  
Tris hexafluoroacetylacetonato europium bisdiphenylphosphinoethane bis P-oxide adduct  
Tris hexafluoroacetylacetonato europium bisdiphenylphosphinopropane bis P-oxide adduct  
Tris hexafluoroacetylacetonato europium bisdiphenylphosphinobutane bis P-oxide adduct  
Tris hexafluoroacetylacetonato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct  
Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato europium triphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato europium tritolylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato europium 1-naphthylidiphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato europium triphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato europium tritolylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato europium 1-naphthylidiphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato europium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato europium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato europium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato europium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris acetylacetonato samarium triphenylphosphine oxide adduct

Tris acetylacetonato samarium tritolylphosphine oxide adduct

Tris acetylacetonato samarium 1-naphthylidiphenylphosphine oxide adduct

Tris acetylacetonato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris acetylacetonato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris acetylacetonato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris acetylacetonato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris dibenzoylmethanato samarium triphenylphosphine oxide adduct

Tris dibenzoylmethanato samarium tritolylphosphine oxide adduct

Tris dibenzoylmethanato samarium 1-naphthylidiphenylphosphine oxide adduct

Tris dibenzoylmethanato samarium bisdiphenylphosphinoethane bis P-oxide adduct  
Tris dibenzoylmethanato samarium bisdiphenylphosphinopropane bis P-oxide adduct  
Tris dibenzoylmethanato samarium bisdiphenylphosphinobutane bis P-oxide adduct  
Tris dibenzoylmethanato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct  
Tris thenoyltrifluoroacetato samarium triphenylphosphine oxide adduct  
Tris thenoyltrifluoroacetato samarium tritolylphosphine oxide adduct  
Tris thenoyltrifluoroacetato samarium 1-naphthyldiphenylphosphine oxide adduct  
Tris thenoyltrifluoroacetato samarium bisdiphenylphosphinoethane bis P-oxide adduct  
Tris thenoyltrifluoroacetato samarium bisdiphenylphosphinopropane bis P-oxide adduct  
Tris thenoyltrifluoroacetato samarium bisdiphenylphosphinobutane bis P-oxide adduct  
Tris thenoyltrifluoroacetato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct  
Tris 2,2,6,6-tetramethylheptanedionato samarium triphenylphosphine oxide adduct  
brightness=1  
Tris 2,2,6,6-tetramethylheptanedionato samarium tritolylphosphine oxide adduct  
Tris 2,2,6,6-tetramethylheptanedionato samarium 1-naphthyldiphenylphosphine oxide adduct  
Tris 2,2,6,6-tetramethylheptanedionato samarium bisdiphenylphosphinoethane bis P-oxide adduct  
Tris 2,2,6,6-tetramethylheptanedionato samarium bisdiphenylphosphinopropane bis P-oxide adduct  
Tris 2,2,6,6-tetramethylheptanedionato samarium bisdiphenylphosphinobutane bis P-oxide adduct  
Tris 2,2,6,6-tetramethylheptanedionato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct  
Tris 3-methylpentane-2,4-dionato samarium triphenylphosphine oxide adduct  
Tris 3-methylpentane-2,4-dionato samarium tritolylphosphine oxide adduct  
Tris 3-methylpentane-2,4-dionato samarium 1-naphthyldiphenylphosphine oxide adduct  
Tris 3-methylpentane-2,4-dionato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato samarium triphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato samarium tritolylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato samarium 1-naphthyldiphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris pivaloyltrifluoroacetato samarium triphenylphosphine oxide adduct

Tris pivaloyltrifluoroacetato samarium tritolylphosphine oxide adduct

Tris pivaloyltrifluoroacetato samarium 1-naphthyldiphenylphosphine oxide adduct

Tris pivaloyltrifluoroacetato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris pivaloyltrifluoroacetato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris pivaloyltrifluoroacetato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris pivaloyltrifluoroacetato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris trifluoroacetylacetato samarium triphenylphosphine oxide adduct

Tris trifluoroacetylacetato samarium tritolylphosphine oxide adduct

Tris trifluoroacetylacetato samarium 1-naphthyldiphenylphosphine oxide adduct

Tris trifluoroacetylacetato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris trifluoroacetylacetonato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris trifluoroacetylacetonato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris trifluoroacetylacetonato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris hexafluoroacetylacetonato samarium triphenylphosphine oxide adduct

Tris hexafluoroacetylacetonato samarium tritolylphosphine oxide adduct

Tris hexafluoroacetylacetonato samarium 1-naphthyldiphenylphosphine oxide adduct

Tris hexafluoroacetylacetonato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris hexafluoroacetylacetonato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris hexafluoroacetylacetonato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris hexafluoroacetylacetonato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato samarium triphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato samarium tritolylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato samarium 1-naphthyldiphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato samarium triphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato samarium tritolylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato samarium 1-naphthyldiphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato samarium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato samarium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato samarium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato samarium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris acetylacetonato dysprosium triphenylphosphine oxide adduct

Tris acetylacetonato dysprosium tritolylphosphine oxide adduct

Tris acetylacetonato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris acetylacetonato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris acetylacetonato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris acetylacetonato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris acetylacetonato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris dibenzoylmethanato dysprosium triphenylphosphine oxide adduct

Tris dibenzoylmethanato dysprosium tritolylphosphine oxide adduct

Tris dibenzoylmethanato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris dibenzoylmethanato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris dibenzoylmethanato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris dibenzoylmethanato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris dibenzoylmethanato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris thenoyltrifluoroacetonato dysprosium triphenylphosphine oxide adduct

Tris thenoyltrifluoroacetonato dysprosium tritolylphosphine oxide adduct

Tris thenoyltrifluoroacetonato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris thenoyltrifluoroacetonato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris thenoyltrifluoroacetonato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris thenoyltrifluoroacetonato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris thenoyltrifluoroacetato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato dysprosium triphenylphosphine oxide adduct  
brightness=4

Tris 2,2,6,6-tetramethylheptanedionato dysprosium tritolylphosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 2,2,6,6-tetramethylheptanedionato dysprosium  
diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 3-methylpentane-2,4-dionato dysprosium triphenylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato dysprosium tritolylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris 3-methylpentane-2,4-dionato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-methylpentane-2,4-dionato dysprosium  
diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato dysprosium triphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato dysprosium tritolylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris 3-ethylpentane-2,4-dionato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 3-ethylpentane-2,4-dionato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris pivaloyltrifluoroacetato dysprosium triphenylphosphine oxide adduct

Tris pivaloyltrifluoroacetato dysprosium tritolylphosphine oxide adduct

Tris pivaloyltrifluoroacetato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris pivaloyltrifluoroacetato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris pivaloyltrifluoroacetato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris pivaloyltrifluoroacetato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris pivaloyltrifluoroacetato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris trifluoroacetylacetonato dysprosium triphenylphosphine oxide adduct

Tris trifluoroacetylacetonato dysprosium tritolylphosphine oxide adduct

Tris trifluoroacetylacetonato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris trifluoroacetylacetonato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris trifluoroacetylacetonato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris trifluoroacetylacetonato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris trifluoroacetylacetonato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris hexafluoroacetylacetonato dysprosium triphenylphosphine oxide adduct

Tris hexafluoroacetylacetonato dysprosium tritolylphosphine oxide adduct

Tris hexafluoroacetylacetonato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris hexafluoroacetylacetonato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris hexafluoroacetylacetonato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct



Tris hexafluoroacetylacetonato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris hexafluoroacetylacetonato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato dysprosium triphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato dysprosium tritolylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedionato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato dysprosium triphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato dysprosium tritolylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato dysprosium 1-naphthyldiphenylphosphine oxide adduct

Tris 1-phenyl-1,3-butanedionato dysprosium bisdiphenylphosphinoethane bis P-oxide adduct

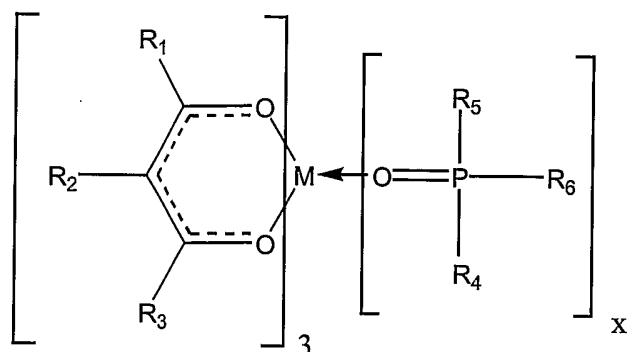
Tris 1-phenyl-1,3-butanedionato dysprosium bisdiphenylphosphinopropane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato dysprosium bisdiphenylphosphinobutane bis P-oxide adduct

Tris 1-phenyl-1,3-butanedionato dysprosium diphenyl(triphenylphosphinaza)phosphine oxide adduct

Claims

## 1. Compounds of formula I:



Formula I

wherein

x is 1 or 2

M is selected from Europium, Terbium, Dysprosium and Samarium;

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are independently of each other selected from phenyl, naphthyl, H and C<sub>1</sub>-C<sub>6</sub> branched or straight chain alkyl, thiophene and C<sub>1</sub>-C<sub>6</sub> fluorinated alkyl wherein the fluorination may be in 1 or all positions or any intermediate value, substituted phenyl wherein the substituents are independently selected from C<sub>1</sub>-C<sub>4</sub> straight or branched chain alkyl, Cl, Br, F, I and the phenyl group may be substituted in 1, 2 or 3 positions;

R<sub>4</sub> and R<sub>5</sub> are independently of each other selected from phenyl, tolyl, naphthyl, C<sub>1</sub>-C<sub>6</sub> branched or straight chain alkyl and substituted phenyl wherein the substituents are independently selected from C<sub>1</sub>-C<sub>4</sub> straight or branched chain alkyl and the phenyl group may be substituted in 1, 2 or 3 positions;

R<sub>6</sub> is selected from phenyl, tolyl, naphthyl, C<sub>1</sub>-C<sub>6</sub> branched or straight chain alkyl,  $-(CH_2)_nP(O)R_7R_8$ , wherein n=1 to 4 and  $-N=P(O)R_7R_8R_9$ , wherein R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are independently selected from phenyl, naphthyl, C<sub>1</sub>-C<sub>6</sub> branched or straight chain alkyl and substituted phenyl wherein the substituents are independently selected from C<sub>1</sub>-C<sub>4</sub> straight or branched chain alkyl and the phenyl group may be substituted in 1, 2 or 3 positions;

R<sub>6</sub> is also selected from substituted phenyl wherein the substituents are independently selected from C<sub>1</sub>-C<sub>4</sub> straight or branched chain alkyl and the phenyl group may be substituted in 1, 2 or 3 positions.

2. A compound according to claim 1 wherein when R6 is  $-(\text{CH}_2)_n\text{P}(\text{O})\text{R}_7\text{R}_8$  then the O is coordinated to the M group.
3. A compound according to claim 1 wherein when R6 is  $-(\text{CH}_2)_n\text{P}(\text{O})\text{R}_7\text{R}_8$  then the O is coordinated to another equivalent metal atom as a bridging group.
4. A compound according to any of claims 1-3 wherein  
R1, R2 and R3 are independently of each other selected from phenyl, and C1-C4 branched or straight chain alkyl,  
R4 and R5 are independently of each other selected from phenyl, tolyl and C1-C6 branched or straight chain alkyl,  
R6 is selected from phenyl, tolyl, C1-C6 branched or straight chain alkyl, and 2-diphenylphosphinoxyethyl.
5. Use of a compound according to any of claims 1-4 as a triboluminescent material.
6. A method of making paper that emits light when torn and/or pressed and/or gripped and/or folded comprising the steps of coating and/or impregnating the paper with triboluminescent material given by claims 1-3.
7. A method according to claim 6 wherein the triboluminescent material is applied by one or more of the following methods:
  - in an adhesive composition, and/or in an encapsulant;
  - in a solvent followed by solvent evaporation;
  - by melting the triboluminescent material such that it soaks into the paper;
  - by incorporating the triboluminescent material together with the pulp, fibre during manufacture of the paper.

8. A method according to claim 7 wherein the triboluminescent material is applied in an adhesive composition and/or in an encapsulant wherein the encapsulant is a polymer which is selected from the following:

acrylic and methacrylic resins, polyimides, polyamides, melamine/formaldehyde resins, urea formaldehyde resins, epoxy resins, poly(p-xylylene), gelatin, poly(lactic acid), polyester resins and alkyd resins.

9. A method according to claim 7 wherein the triboluminescent material is applied in an adhesive composition and/or in an encapsulant wherein the adhesive composition may also comprise one or more of the following:

solvents, dispersants, plasticisers, curing agents, dyes, fillers, stabilisers, anti-oxidants.

10. Paper comprising one or more triboluminescent materials given by claims 1-3 such that the paper triboluminesces when the paper is torn and/or pressed and/or gripped and/or folded.

11. A product comprising the paper of claim 10.

12. An adhesive composition comprising an adhesive and one or more triboluminescent materials according to claims 1-3.

13. A method of adhering two surfaces together comprising the steps of: applying an adhesive composition to one or more surfaces and bringing the surfaces into contact such that adhesion occurs wherein the adhesive composition comprises an adhesive and one or more triboluminescent materials given by claims 1-3.

14. A method of making adhesive tape that flashes when used comprising the steps of:

selecting a substantially transparent substrate,  
optionally depositing an adhesion promoter on the substrate,  
depositing an adhesive composition comprising a triboluminescent material given by claims 1-3 on to the substrate,  
optionally drying the adhesive composition,  
optionally depositing a further laminating sheet on top of the adhesive composition before or after any drying stage.

15. A method for detecting tampering of a sealed article comprising the steps of:  
coating a part of an unsealed article with an adhesive composition,  
sealing the article,  
wherein the adhesive composition further comprises one or more triboluminescent materials given by claims 1-3 such that on breaking the seal triboluminescence will be observed.

16. A damage-sensing device comprising at least one light sensor and at least one triboluminescent material given by claims 1-3.

Fig.1.

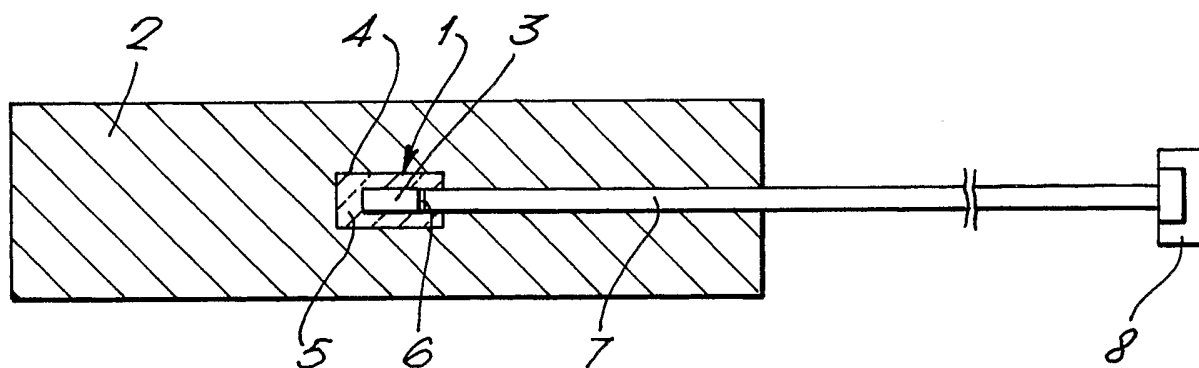


Fig.2.

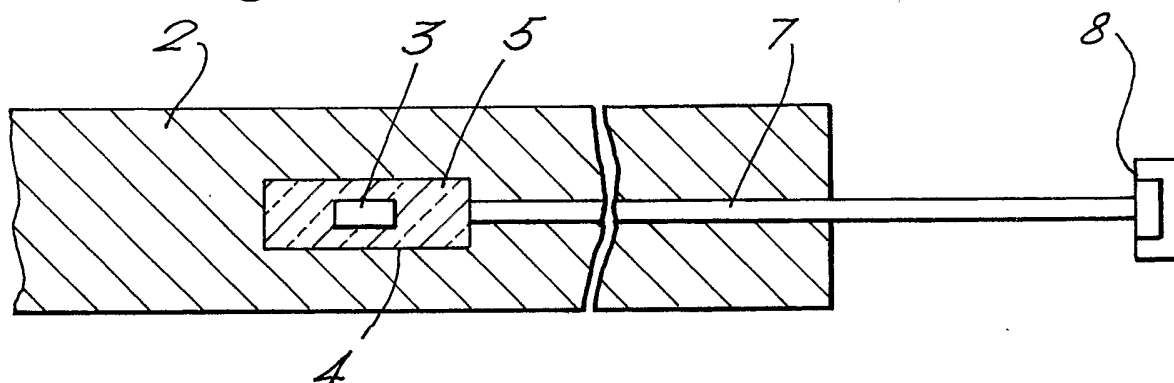


Fig.3.

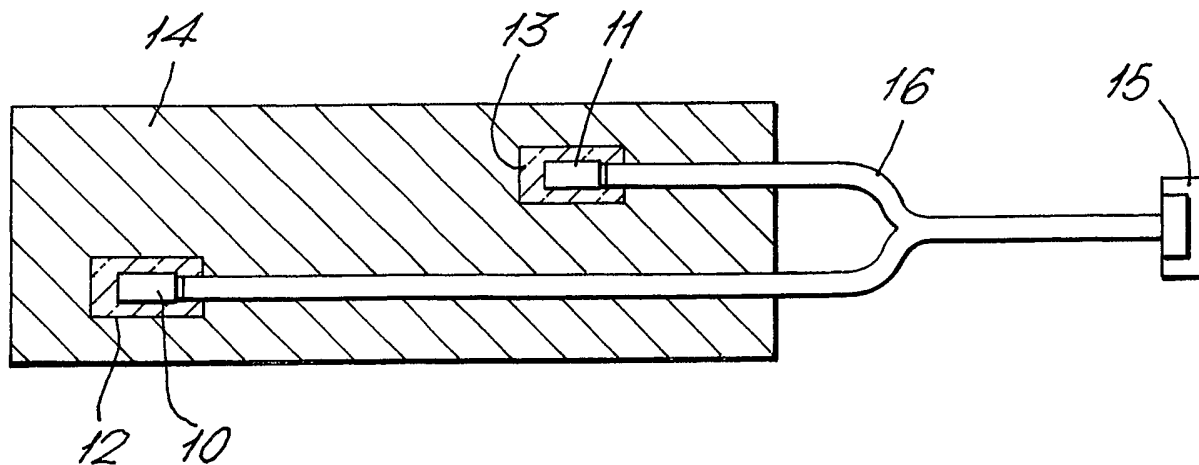


Fig.4.

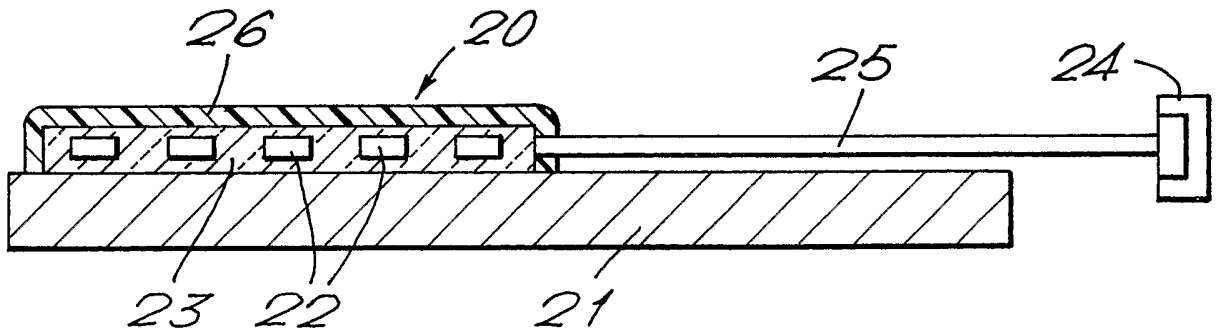


Fig.5.

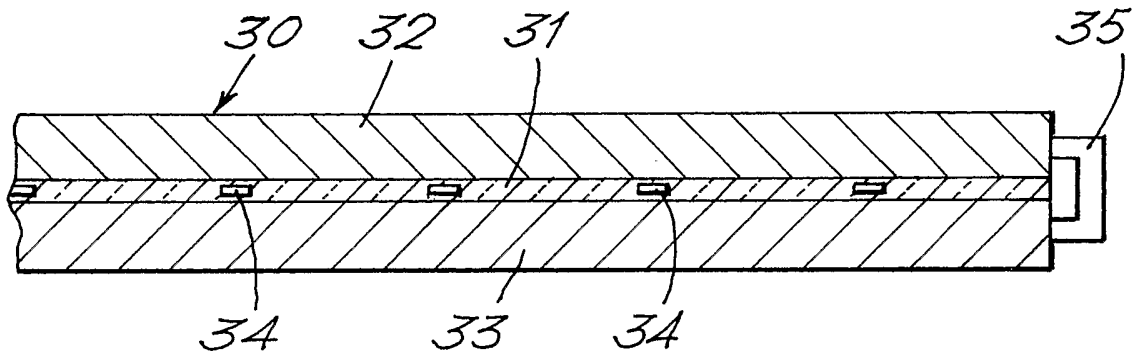


Fig.6.

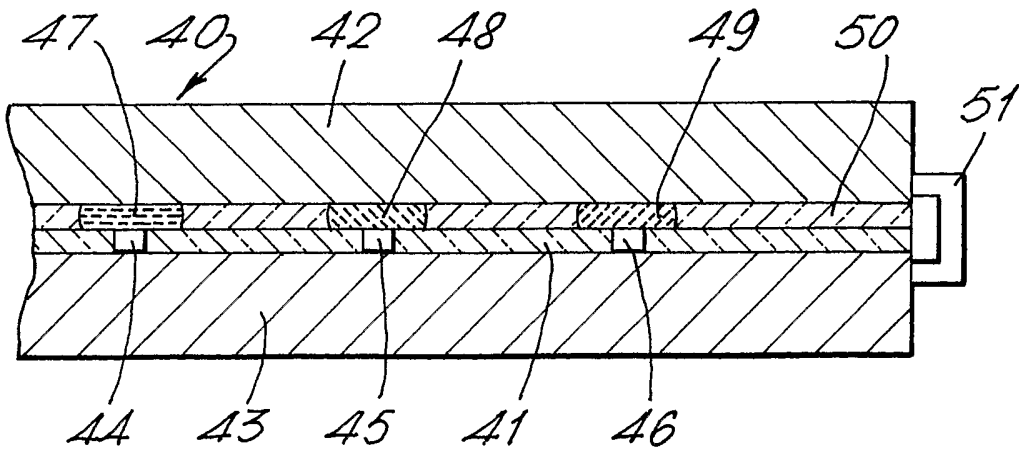
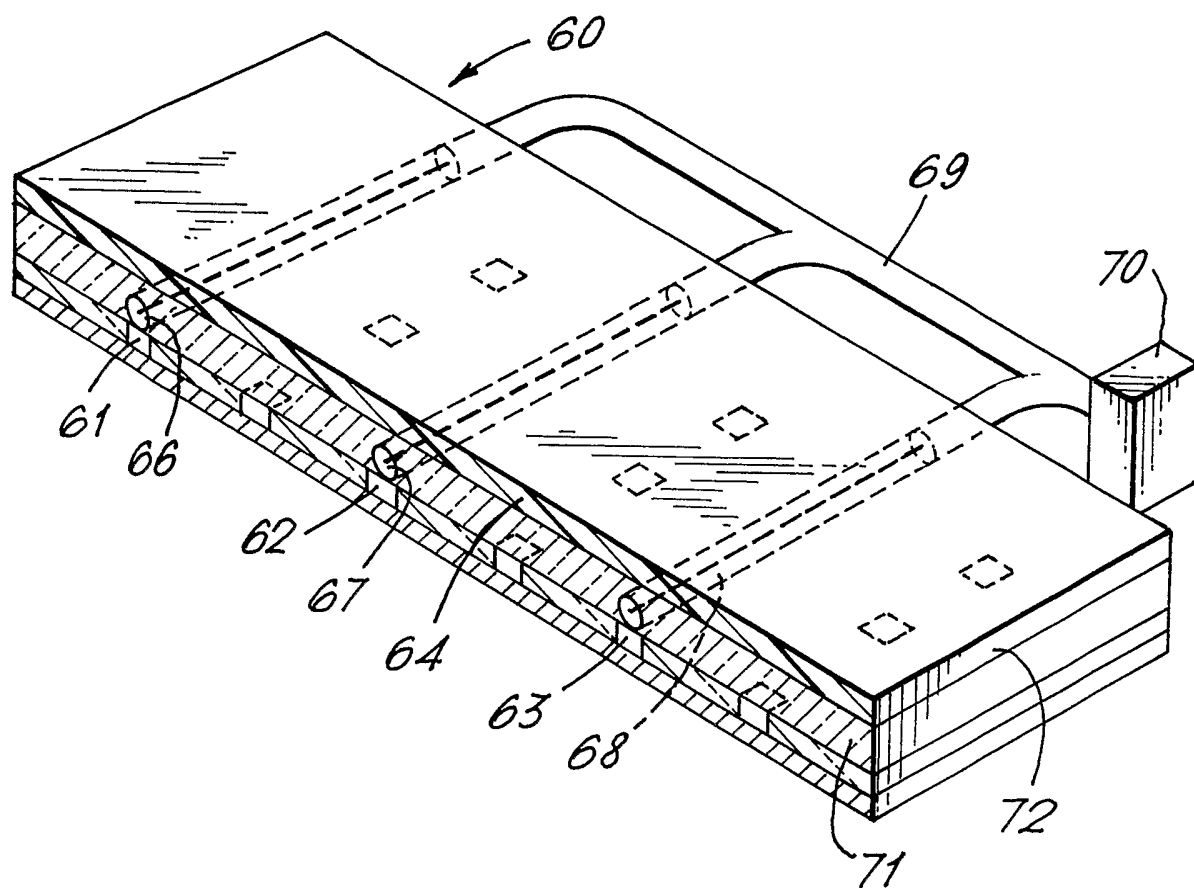


Fig.7.





## INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K11/06 G01N23/00 G09F13/20 B42D15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K G01N G09F B42D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, CHEM ABS Data, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Date of the actual completion of the international search

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Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

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Doslík, N

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