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(56) Documents cited
GB 0650459 A EP 0092240 A US 4586811 A

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(54) Anti-Stokes luminescent material

(57) An anti-Stokes luminescent material is prepared from a fused mixture of rare earth compounds and, if necessary, other components, is in the form of particles no more than 40 μm in size and has substantially the same luminescence as the fused mixture. The material is preferably doped with yttrium oxysulphide, and is used in inks.

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LUMINESCENT MATERIALS AND THEIR PREPARATION

This invention relates to materials that can be used, for example, as markers for authenticating items such as security documents, and to their preparation.

Luminescent materials such as fluorescent and phosphorescent materials are commonly used in banknotes and the like for security verification purposes. The commercially-used luminophors obey Stokes Law, in that their emissions are at a lower energy than that of the exciting radiation. For example, such materials when illuminated with ultraviolet radiation will emit in the visible.

Anti-Stokes or, as they are otherwise known, "upconverting" materials emit light (visible or ultraviolet) which has a shorter wavelength than the activating radiation. For the purpose of this specification, Anti-Stokes materials absorb infrared radiation, typically from 700 to 1300 nm, and emit in the visible. Anti-Stokes materials emit photons at higher energy, and this can arise if two or more incident photons result in one emitted photon (of higher energy). Anti-Stokes materials have seen limited application to security items.

Inorganic luminescent pigments are normally refractory solids and, if the particle size is reduced by grinding, then their luminescent efficiency decreases rapidly, as is well known. Unfortunately, the smallest acceptable anti-Stokes particle size previously available is much larger than is normally acceptable for security printing inks. It has not hitherto been possible to make satisfactory ink formulations which contain anti-Stokes materials suitable for the main security printing methods, i.e. intaglio, letterpress or lithography, owing to their requirement for small particles.

For use in currency, particularly severe demands are placed on inks. The inks must retain their properties for the life of the document, withstanding the rigours and challenges of handling, wetting and contamination. Similarly stringent properties must also apply to other security documents which have a long life and whose value is associated with the integrity of the document.

Security documents by their very nature need to incorporate a variety of different measures in order to defeat counterfeiting. At one extreme, visual measures are designed to be seen with the naked eye. At the other extreme, sophisticated and expensive detectors may be employed, say attached to banknote sorting equipment, to validate banknotes and the like. Many of these features may be invisible under normal viewing conditions.

US-A-4047033 discloses documents including anti-Stokes fluoride materials. Such materials are generally unsuitable for security documents, however, since they are liable to hydrolysis which causes a reduction of their luminescence, and because they are difficult to produce in finely particulate form, i.e. less than 20 μm in size. The particles disclosed in US-A-4047033 are adapted for screen inks, and are therefore relatively large.

GB-A-2089385 discloses ferrite, perovskite and garnet-type storage phosphor materials for security documents that absorb in the IR, emitting in the UV.

AU-A-0562509 and AU-A-0571276 describe fluoride, oxide or mixed rare earth oxyfluoride anti-Stokes luminescent materials and their use in security documents. Inks are not described. Some of such materials are liable to hydrolysis; they are difficult to reduce to a suitably small particle size while maintaining fluorescence efficiency. The former document discloses precipitation, sieving and crushing, to obtain small particles.

US-A-4387112 discloses credit cards marked with inorganic storage phosphors, e.g. a mixed phosphor such as SrS(Eu,Sm). They are used in finely-divided form, apparently after grinding. The luminescent properties of almost all phosphors are adversely affected by grinding.

According to the present invention, an anti-Stokes luminescent material comprises a doped rare earth compound that is in the form of particles no greater than 40 μm in size and whose luminescence is substantially at least the same as that of a fused mass of the component compounds.

A material of the invention is in the form of particles which are suitable for use in printing by intaglio, letterpress or offset lithography. For this purpose, the particles have a maximum diameter of no more than 40 μm, more preferably no more than 20 μm, and most preferably below 10 μm, e.g. 1 to 5 μm or even 1 to 2 μm. Particles of such a size can be produced, without grinding, by a process in which, for a doped rare earth oxysulphide, oxides of the rare earths are fused with sulphides or elemental sulphur, the fused mass is leached with water to extract soluble residues, and dried as a powder. Some milling may then be appropriate, depending on the desired particle size.

Although, more generally, the invention relates to any anti-Stokes material that is prepared from a fused mixture of rare earth compounds and, if necessary, other components, a particularly suitable material is doped yttrium oxysulphide, in which the dopants comprise, by weight of the oxysulphide, 4 to 50% of one or more of Er, Yb and Ho, and 1 to 50 ppm of one or more other lanthanide elements. Such a material is described in another Patent Application filed in the name of Thomas De La Rue and Company Ltd and on the same day, entitled "Luminescent Materials and Their use in Security Documents".

The oxysulphide described in the copending Application has the general chemical composition $Y_2O_2S:A$, where A is a primary rare earth dopant selected from Yb, Er or a mixture of Yb and Er. One such composition, i.e. $Y_2O_2S:Yb,Er$, is usually characterised by green emission on IR stimulation.

The total level of doping is generally no more than 30%, and typically less than 25%. For example, the material comprises 2 to 10% Er and 5 to 15% Yb. The weight ratio of Yb to Er may be approximately 1:3.

Other rare earth elements can have a marked effect on luminescent properties, even when present in very small amounts. The amounts of these elements present must be carefully controlled. In the case of Y_2O_2S:Yb,Er, good results may be achieved if one or more of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy is present in an amount of less than 3 ppm and, in certain instances, less than 1 ppm. Higher levels of Ho, Tm and Lu can improve luminescent efficiency, e.g. when present at 2-20 ppm.

The purity of the starting materials will determine the performance of the product. It is preferred to use at least 99.999% pure yttrium oxide, and 99.99% pure ytterbium and erbium oxides.

The doped oxysulphide may be prepared by firing a blend of, say, BDH Chemicals Ltd. AnalaR quality flux materials with pure yttrium oxide, ytterbium oxide and erbium oxide, e.g. at 1100°C for 1 hour. The firing time and temperature may be varied within the ranges 0.5 to 4 hours and 1000 to 1200°C, while 1050-1150°C and 1-2 hours give consistent results. A firing schedule of 1 hour at 1100°C is suitable on this scale.

The ratio of ytrrium : ytterbium : erbium in the blend, before firing, may be varied. Some increase in brightness may be obtained by adjusting the ytterbium content.

The value of the materials used in the present invention includes their stability and their high anti-Stokes efficiency. They are therefore useful as markers in security documents, for preventing counterfeiting.

Security items are items whose value is established or increased by being difficult to counterfeit or alter fraudulently. Examples of security documents, which may incorporate materials of the invention, are banknotes, currency, share certificates, bonds, passports, driving licences, permits, travel tickets, lottery tickets, plastic credit cards, charge cards, cash withdrawal cards, cheque cards, travellers' cheques and bank cheques, smart cards and remote access control cards.

A security document incorporating a material of the invention may conveniently be prepared by applying an ink containing the material. The security printed item may be a banknote.

The ink will normally be used to print, by letter press, intaglio or offset, invisible designs and security features. Alternatively, the materials may be incorporated into coloured inks, to enhance the anti-counterfeiting level of the printing. This may be done, for example, by incorporating the material into a banknote-numbering ink.

Intaglio and letterpress inks are preferred. Letterpress can achieve 5 μm of ink film. Intaglio ink printing can give printed thicknesses of, say, 5 to 70 μm.

An ink of the invention comprises, in addition to the anti-Stokes material, conventional components such as a colourant and a vehicle. For example, the ink may be prepared by thoroughly mixing an extender, wax, anti-Stokes material and any other security additives with resins components of an ink vehicle, and a hydrocarbon solvent. These components are then further dispersed, typically using a triple-roll mill, at a suitable pressure. Once the correct degree of dispersion has been reached, further solvent and other components may be added.

A security document of the invention may be authenticated by irradiation with infrared light, and observation of the visible light thus produced. The means of irradiation may be, for example, a near infrared-emitting gas laser, laser diode or infrared-emitting diode. Laser diodes or infrared emitting diodes, for example GaAs(Si) emitting at 940 nm, may conveniently be employed with matching materials. Alternatively, tungsten-halogen light sources, suitably filtered to remove visible light, may be used.

The materials of the invention have relatively narrow absorption and emission bands. The emission of the illuminating source must therefore be matched to the absorbance of the material and, in the case of machine-reading, this must be matched to the detector. Photodetectors tend to have a wide absorption band which may be narrowed by the use of filters or spectral discriminators.

For the purposes of this specification, the ultraviolet, visible and infrared regions cover from 200 to 399 nm, 400 to 699 nm, and 700 to 1300 nm, respectively. The printed ink may be viewed by exposure with an infrared diode emitting at approximately 940 nm (peak wavelength).

Materials of the invention normally will exhibit a shift of at least 100 nm from the illuminating source, and preferably of 200 nm or more. For example, on irradiation with an infrared diode emitting at a peak wavelength around 940 nm, it is possible to observe orange, green, yellow-orange fluorescences.

An advantage of the invention is that it is not obvious from visible examination of the, say, intaglio printing that the printing has an infrared responsive emitter. The effect is not obvious in its own right, and there are of course many possible physical effects which might be used. Such an effect is therefore deeply hidden, and it will therefore not be readily detectable by a potential counterfeiter.

In order to disguise the effect of those materials which do not themselves luminesce on exposure to ultraviolet illumination, it is possible to mix normal (Stokes) luminophors with the anti-Stokes material. In certain cases, an IR-activated anti-Stokes luminophor which emits in the visible may cause a fluorescent material of emitting absorbance to emit at a longer wavelength.

A particulate material of the invention has substantially the same luminescence, at a given wavelength, as the fused mixture of compounds from which it may be prepared. The loss of luminescence is preferably no more than 50%, and more preferably no more than 25%.

The following Examples illustrate the invent.on. "3N's Grade" and "4N's Grade" indicate a purity of respectively 99.9% and 99.99%.

Example 1

The following materials were milled together in a pint size porcelain mill jar with porcelain balls for 2 hours:

78.74 g	yttrium oxide (3N's grade)
14.96 g	ytterbium oxide (4N's grade)
6.30 g	erbium oxide (4N's grade)
250 ml	water

After milling, the porcelain balls were separated from the slurry of rate earth oxides, the latter was filtered and the mixed rare earth oxides were dried and then sieved.

20 g of this mixed oxide powder was intimately mixed with:

7.48 g	potassium fluoride
5.52 g	sodium carbonate
5.52 g	sulphur

and heated at 1100°C for 1 hour in a covered alumina crucible. When cool, the fused mass was soaked in water until it softened down to a fine powder which was then filtered off, washed with more water, dried and sieved. This material, on irradiation with IR, emitted green radiation. The material was then milled.

The particle size was determined microscopically and at least 90% of the particles had a maximum diameter of less than 40 μm.

In addition to using the purest available components, the crucible was of recystallised alumina. Contamination was avoided wherever possible.

Ytrrium oxysulphide phosphors are usually fairly resistant to grinding, but can be prepared in fine particle size ranges. Milling can be used to reduce the particle size further but generally such grinding is avoided if possible.

<u>Examples 2 to 5</u>

Doped yttrium oxysulphide phosphors were prepared by the procedure of Example 1. In Example 3, the oxide was of Norwegian origin and supplied by Berkshire Ores Ltd as their "phosphor grade". In Example 4, the oxide was supplied by The Propane Company, as their "phosphor grade". In Examples 2 and 5, the oxides were from different suppliers.

The rare earth compositions were determined by using an inductively-coupled plasma atomic emission spectrometer and an inductively-coupled plasma mass spectrometer. The results are tabulated below:

Element	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Y	58.9%	61.1%	61.2%	59.9%
Er	4.73%	4.87%	4.83%	4.85%
Yb	12.8%	11.0%	10.9%	10.8%
Ho	17.3 ppm	<1 ppm	<1 ppm	<1 ppm
Tm	7.5 ppm	<1 ppm	<1 ppm	4.7 ppm
Lu	8.2 ppm	3.1 ppm	2.5 ppm	4.8 ppm

In each case, the La, Gd, Tb and Dy content was each less than 1 ppm, the Nd, Sa and Eu content was each less than 2 ppm, and the Ce and Pr content each less than 3 ppm. The sulphur content (11.75%) for Example 2 was determined separately, and the oxygen content (11.82%) by subtraction.

Particle size determination was made by optical microscopy taking the maximum diameter of the particles and assessing an approximate distribution range and average particle size.

Results are as follows (all values in μm):

Example No.	Number Average	Majority (>50%)	Maximum	Maximum
2	13	5-20	30	5
3	15	10-20	35	5
4	11	6-12	26	4
5	13	6-18	30	4

These sizes are those which result from the preparation without milling. Normally some milling is carried out to reduce the particle range, especially to reduce the size of the larger particles so that the material may be incorporated in an ink formulation. For the above letterpress ink formulations are prepared. These is no significant reduction in luminosity on milling.

CLAIMS

1. An anti-Stokes luminescent material as prepared from a fused mixture of rare earth compounds and, if necessary, other components, that is in the form of particles no more than 40 μm in size and that has substantially the same luminescence as the fused mixture.

2. A material according to claim 1, which comprises doped yttrium oxysulphide.

3. A material according to either preceding claim, in which the average size of the particles is no more than 20 μm.

4. A material according to claim 3, in which the average size of the particles is 1 to 10 μm.

5. An ink comprising a material according to any preceding claim, a vehicle and, optionally, a colourant.

6. A security document or authenticated item bearing a material according to any of claims 1 to 4.

7. A method for preparing a material according to any of claims 1 to 4, which comprises leaching the fused mixture with water to extract soluble residues and, if necessary, milling the precipitated product.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number

9117543.0

Relevant Technical fields

(i) UK Cl (Edition K) C45

(ii) Int Cl (Edition 5) C09K

Search Examiner

DR D ELSY

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Date of Search

8 APRIL 1992

Documents considered relevant following a search in respect of claims 1-7

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X Y	GB 650459 (URBACH) see entire document	X:1,3-5 Y:6
X	EP 0092240 A (FUJI) see especially page 4 line 3 to page 6 line 10	1,3-4
Y	US 4586811 (RICOH) see especially column 5 lines 33-44	6

Category	Identity of document and relevant passages	Rele .t to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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