GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 144365 dated 2nd August 1978
Application and Provisional Specification No. 1552/Cal/76 dated 9th August 1976
Acceptance of the complete specification advertised on 29th April 1978

Index at acceptance— 121 [L X111(2)]
144A [X11(3)]
International Classification— D 21 h 5/00

" A METHOD FOR MAKING OF LUMINESCENT TRANSFER PAPER "

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1960).

The following specification describes the nature of this invention.

This is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, MOHAMMED IFTIKHAR AHMED SIDDIQI, Scientist, NAGAMONY RAJARAM, Scientist, KANNAM KUMARATH GOPINATHAN, Scientist, RAMAYYER LAKSHMINARAYANAN, Scientist and Miss ALICE KURIAN, Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, all Indian citizens.

PRICE: TWO RUPEES

144365

This invention relates to luminescent transfer paper.

Luminescent transfer paper could be used in a number of applications such as invisible signature verification system, confidential communication system etc., Many other uses will be obvious from the description of the invention.

Hitherto, use of luminescent transfer paper abroad has been reported for instance in invisible writing verification system. However, details for the production of the paper are not available in the literature.

The object of this invention is to provide with a method of making luminescent transfer paper of a high quality for various purposes by a simple and elegant process, at the same time, using all indigenous materials.

To these ends, the invention broadly consists in coating paper sheets with a copying layer ultimately comprising grease, wax, and a luminescent substance which is substantially invisible in ordinary daylight and luminesces when exposed to radiation different from and of higher energy than re-emitted by luminous substances. More usually, the exciting or activating radiation is the ultraviolet of either 3650 Å or 2537 Å, usually obtainable from a mercury vapour lamp and the emitted radiation is in the visible range.

We shall now proceed to describe in greater detail the method of making the luminescent transfer paper of our invention:

The paper is given (i) an initial coating with a solution (I) containing a grease in an organic solvent such as xylene (ii) followed by a coating with a ~~saturated~~ saturated solution (II) containing wax in an appropriate solvent (iii) followed by a coating with a suspension (III) of phosphor in a suitable organic liquid vehicle to which a very small quantity of a suspension agent has been added.

(iv) finally followed by a coating with solution (I), preferred in some cases depending on the phosphor.

Drying and subjecting the paper to mild pressure is done to ensure good transfer quality.

Coatings on to paper which have been done by us using the spraying technique have been found to give good performance. Several phosphors such as zinc sulphides giving various emission colours, calcium tungstate blue phosphor, zinc silicate green phosphor, magnesium fluogermanate red phosphor and calcium halophosphate daylight phosphor could all be used satisfactorily.

Whereas among the materials mentioned by us such as greases, waxes, solvents, suspension agents, different varieties could be used, the particular ones described herein have been found to be more suitable. The phosphors used should have a reasonably fine particle size in the range of 5 - 50 microns. This luminescent transfer paper does not give smudging. The coating is durable and invisible in ordinary light but becomes luminescent under ultraviolet

Having described the manner in which the luminescent transfer paper is prepared, we shall now indicate the mode of its use for a particular application, such as, black light (ultraviolet of long or short wave length) invisible verification system, for instance, in banking. From this description, many more other applications, wherein the luminescent transfer paper could be used with advantage, would become obvious.

One writes 'visibly' with, for instance, a ball point pen on the luminescent transfer paper - the signature is transferred 'invisibly' to any part of the pass book, preferably over a printed area. Signature which does not smudge, and is unaffected by water, is quite durable. The verifier, having a Black ray lamp,

could then, on presentation of the pass book do 'on the spot' or 'at the counter' verification by comparing the 'invisible' signature observed clearly under the Black ray lamp. The comparison signature is otherwise undetected and thus protects against forgery if pass book is lost. This results in a great economy of time and expense.

The description above, of how the special luminescent transfer paper is used, is only illustrative and should be suggestive of many other uses. For instance, the special luminescent transfer paper could also be aptly used in hand writing or typewriting a confidential communication, which could be written on a 'visible' 'original' making an 'invisible' 'copy', which could subsequently be read off under an ultraviolet lamp. This is of interest in defence organisation.

The special luminescent transfer paper could be made comprising different phosphor - radiation systems as required in a particular application, depending on its significance.

The following typical examples are given to illustrate a preferable method of practising the invention.

EXAMPLE 1

Solvent (I) is made with about 0.2 g silicone grease in 100 cc xylene; A saturated Solution (II) is made with paraffin wax in benzene; Suspension (III) is made with 5 gm of phosphor (zinc sulphide: Copper - green in 100 cc of ethyl alcohol with the addition of about a few drops of acetic acid.

Sheets of paper are spray-coated with solutions (I), (II), (III) and (I), in that sequence, allowing a few minutes for somewhat drying of the coated layer between successive coatings and during that time, the paper is subjected also to a mild pressure to stabilise

coating using a roller. A sheet of paper of size about 20 x 30 cm would require about 10 cc each of solution I, II, III and I. The sheets of paper thus coated could be cut and made into books of smaller size if so required by subsequent use. The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 3650°A, when it gives a green luminescence.

EXAMPLE 2

Solutions I, II are made as in example 1

Suspension III is made as in example 1 except for the fact that the phorphor used is zinc sulphide ZnS:Ag blue phosphor.

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 3650°A, when it gives a blue luminescence.

EXAMPLE 3

Solutions I, II are made as in example 1.

Suspension III is made as in example 1 except for the fact that the phosphor used is calcium tungstate $CaWO_4$ blue phosphor.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 2537°A, when it gives a blue luminescence.

EXAMPLE 4

Solutions I, II are made as in example 1.

Suspension III is made as in example 1, except for the fact that the phosphor used is zinc silicate green phosphor (Zn_2SiO_4:Mn)

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 2357°A, when it gives a green luminescence.

EXAMPLE 5

Solutions I, II are made as in example 1.

Suspension III is made as in example 1, except for the fact that the phosphor used in magnesium fluogermanate 3.5 MgO, 0.50 MgF_2 GeO_2:Mn red phosphor.

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 2537°A, when it gives red luminescence colour.

EXAMPLE 6

Solution I, II are made as in example 1.

Suspension III is made as in example 1, except for the fact that the phosphor used is calcium halophosphate 3 $Ca_3(PO_4)_2$, $Ca(F,Cl)_2$:(Sb,Mn) daylight phosphor.

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 2537°A, when it gives a daylight luminescence colour.

EXAMPLE 7

All conditions as in example 1, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 8

All conditions as in example 2, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 9

All conditions as in example 3 except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 10

All conditions as in example 4, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 11

All conditions as in example 5, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 12

All conditions as in example 6, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

ADVANTAGES

The following are among the main advantages of the invention:

1 The method of making luminescent transfer paper is simple and elegant.

2 The materials and equipment are all indigenously available.

3 The process could be used on any reasonably good texture paper

4. The coating is not smudgy, not affected by water and is of high durability over years.

5 The transfer can be effected more than once using a single luminescent transfer paper thus enabling it also to be reused just as a carbon sheet.

6 Several phosphor radiation system could be pressed into service with great facility depending on the particular application.

7 The special luminescent transfer paper resulting from this invention has the prospects of many applications.

Dated this 4th day of August, 1975.

Sd/-
Asstt. Patents Officer,
Council of Scientific & Industrial Research.

144365

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

"A METHOD FOR MAKING OF LUMINESCENT TRANSFER PAPER"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, MOHAMMED IFTIKHAR AHMED SIDDIQI, Scientist, NAGANOMY RAJARAM, Scientist, KANNAM KUMARATH GOPINATHAN, Scientist, RAMAYYER LAKSHMINARAYANAN, Scientist and Miss ALICE KURIAN, Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, all Indian citizens.

144365

This invention relates to a method for the making of luminescent transfer paper for preparing in visible copies of writing.

Luminescent transfer paper could be used in a number of applications such as confidential communication system and invisible signature verification systems. Many other uses will be obvious from the description of the invention.

Hitherto, use of luminescent transfer paper abroad has been reported for instance in invisible writing verification system. However, details for the production of the paper are not available in the literature.

The object of this invention is to provide with a method of making luminescent transfer paper of a high quality for various purposes by a simple and elegant process, at the same time, using all indigenous materials.

To these ends, the invention broadly consists in coating paper sheets with a copying layer ultimately comprising grease, wax, and a luminescent substance which is substantially invisible in ordinary light and luminesces when exposed to radiation different from and of higher energy than re-emitted by luminous substance. More usually, the exciting or activating radiation is the ultraviolet of either 3650 A^{0} or 2537 A^{0} depending on the phosphor, the radiation usually obtainable from a mercury vapour lamp and the emitted radiation is in the visible range.

Accordingly the invention relates to a method for making luminescent transfer paper for preparing invisible copies of writing comprises coating a paper sheet with successive layers of grease, wax, a luminescent substantially which is substantially invisible in ordinary light, drying the paper after each coating operation, subjecting the same to a mild pressure to stabilise the coating using a roller and giving a final coating of grease.

We shall now proceed to describe in greater detail the method of making the luminescent transfer paper of our invention:

The paper is coated in the following sequence:

i) An initial coating with a solution (I) containing a grease in an organic solvent such as xylene;

ii) Coating with a saturated solution (II) containing wax in an appropriate solvent such as benzene;

iii) Coating with a suspension (III) of phosphor in a suitable organic liquid vehicle to which a very small quantity of a suspension agent such as acetic acid has been added

iv) In subsequent experimentation, we have found that a further coating with soltuion (II) tends to enhance the protective character. A slight variation of this coating layer could also comprise 50:50 mixture of grease in xylene and wax in benzene (This solution we shall choose to call IIA, which gives a slightly better performance.

v) A final coating with solution (I).

During and subjecting the paper to mild pressure is done to ensure good quality

Coatings on to paper which have been done by us using the spraying technique have been found to give good performance. Several phosphors such as zinc sulphides giving various emission colours, calcium tungstate blue phosphor, zinc, silicate green phosphor, magnesium fluogermanate red phosphor and calcium halophosphate daylight phosphor could all be used satisfactorily.

Whereas among the materials mentioned by us such as greases, waxes, solvents, suspension agents, different varieties could be used, the particular ones described herein have been found to be more suitable as well as the particular coating sequence used by us. The phsophor used should have a reasonable fine particle size in the range of 5-50 microns. This luminescent transfer paper does not give smudging. The coating is durable and invisible in ordinary light but becomes luminescent under ultraviolet radiations.

Having described the manner in which the luminescent transfer paper is prepared, we shall now indicate the mode of

its use for a particular application, such as, black light (ultraviolet of long or short wave [redacted] length) invisible verification system, for instance, in banking. From this description, many more other applications , wherein the luminescent transfer paper could be used with advantage, would become obvious.

One writes 'visibly' with, for instance, a ball point pen on the luminescent transfer paper - the signature is transferred 'invisibly' to any part of the pass book, preferably over a printed area. Signature which does not smudge, and is unaffected by water, is quite durable. The verifier, having a black ray lamp, could then, on presentation of the pass book do 'on the spot' or 'at the counter' verification by comparing with the 'invisible' signature observed clearly under the Black ray lamp. The comparison signature is otherwise undetected and thus protects against forgery if pass book is lost. This results in a great economy of time and expense.

The description above, of how the special luminescent transfer paper is used, is only illustrative and should be suggestive of many other uses. For instance, the special luminescent transfer paper could also be aptly used in hand writing or typewriting a confidential coounication, which could be written on a 'visible' 'original' making an 'invisible' copy', which could subsequently be read off under an ultraviolet lamp. This is of interest in defenfe organisation.

The transfer, can be effected a number of times using a sibgle luminescent transfer paper thus enabling it to be re-used just as in the case of a carbon paper. The coating is not smudgy, not affected by water.

The special luminescent transfer paper could be made comprising different phosphor-radiation systems as required [redacted] in a particular application, depending on its significance.

Both the luminescent transfer paper and the 'invisible' message written employing the same, have, both, very durable keeping quality extending over years. It has also been found that 'burning' of the luminescent transferred message still leaves the message impression readable if delicately handled; this could be of great significance in some special situations.

The following typical examples are given to illustrate a preferable method of practising the invention.

EXAMPLE 1

Solution (I) is made with about 0.2 g silicone grease in 100 cc xylene; a saturated solution (II) is made with paraffin wax in benzene; suspension (III) is made with 5 gm of phosphor (zinc sulphide: copper-green) in 100 cc of ethyl alcohol with the addition of about a few drops of acetic acid.

Sheets of paper are spray-coated with solutions (I), (II), (III), and (I), in that sequence, allowing a few minutes for somewhat drying of the coated layer between successive coatings and during that time, the paper is subjected also to a mild pressure to stabilise coating using a roller. A sheet of paper of size about 20 x 30 cm would require about 10 cc each of solution I, II, III and I. The sheets of paper thus coated could be cut and made into books of smaller size if so required by subsequent use. The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 3650 Å, when it gives a green luminescence.

EXAMPLE 2

Solutions I, II are made as in example 1.

Suspension III is made as in example I, except for the fact that the phosphor used is zinc sulphide ZnS:Ag blue phosphor.

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 3650 Å, when it gives a blue luminescence.

EXAMPLE 3

Solutions I, II are made as in example 1.

Suspension III is made as in example 1 except for the fact that the phosphor used is calcium tungstate $CaWO_4$ blue phosphor.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 2537 Å, when it gives a blue luminescence.

EXAMPLE 4

Solutions I, II are made as in example 1.

Suspension III is made as in example 1, except for the fact that the phosphor used is zinc silicate green phosphor (Zn_2SiO_4:Mn).

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 2537 Å, when it gives a green luminescence.

EXAMPLE 5

Solutions I, II are made as in example 1.

Suspension III is made as in example 1, except for the fact that the phosphor used is magnesium fluogermanate 3.5 MgO, 0.50 MgF_2, GeO_2:Mn red phosphor.

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer excited by ultraviolet of 2537 Å or 3650 Å when it gives red luminescence colour.

EXAMPLE 6

Solutions I, II are made as in example 1.

Suspension III is made as in example 1, except for the fact that the phosphor used is calcium halophosphate 3 $Ca_3(PO_4)_2$, $Ca(F,Cl)_2$: (Sb, Mn) daylight phosphor.

Coating is done as in example 1.

The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 2537 Å, when it gives a daylight luminescence colour.

EXAMPLE 7

All conditions as in example 1, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 8

All conditions as in example 2, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 9

All conditions as in example 3 except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 10

All conditions as in example 4, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 11

All conditions as in example 5, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 12

All conditions as in example 6, except for the fact that in making solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 13

Solution (I) is made with about 0.2 gm. Silicone grease in 100 cc xylene; a saturated solution (II) is made with

paraffin wax in benzene, suspension (III) is made with 5 gms of phosphor, zinc sulphide: copper-green, in 100 cc of ethyl alcohol with the addition of about a few drops of acetic acid.

Sheets of paper were spray-coated with solutions (I), (II), (III), (II) and (I) in that sequence, allowing a few minutes for somewhat drying of the coated layer between successive coating and during that time, the paper is subjected also to a mild pressure to stabilise coating using a roller. A sheet of paper of size about 20 x 30 cm would require about 10 cc each of solution I, II, III and I. The sheets of paper thus coated could be cut and made into books of smaller size if required by subsequent use. The luminescent transfer paper thus made gives a transfer mainly excited by ultraviolet of 3650 Å when it gives a green luminescence.

EXAMPLE 14

All other conditions as in example 13 except that of making suspension (III), the phosphor used is zinc sulphide Ag blue phosphor (excitable by 3650 Å).

EXAMPLE 15

All other conditions as in example 13 except that in making suspension (III) the phosphor used is calcium tungstate blue (excitable by 2537 Å).

EXAMPLE 16

All other conditions as in example 13 except that in making suspension (III), the phosphor used is zinc silicate:Mn, green (excitable by 2537 Å).

EXAMPLE 17

All other conditions as in example 13 except that in making suspension (III) the phosphor used is magnesium fluogermanate: Mn, red (excitable by 2537 Å or 3650 Å).

EXAMPLE 18

All other conditions as in example 13 except that in making suspension (III), the phospher used is calcium halophosphate; Sb, Mn-daylight (excitable by 2537 Å).

EXAMPLE 19

All conditions as in example 13 except that in solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 20

All conditions as in example 14, except that in solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 21

All conditions as in example 15, except that in solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 22

All conditions as in example 16, except that in solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 23

All conditions as in example 17, except that in solution (II), paraffin wax is replaced by carnauba wax.

EXAMPLE 24

All conditions as in example 18, except that in solution (II), paraffin wax is replaced by carnauba wax.

ADVANTAGES

The following are among the main advantages of the invention:

1 The method of making luminescent transfer paper is simple and elegant.

2 The materials and equipment are all indigenously available.

3. The process could be used on any reasonibly good texture paper.

4 The coating is not smudgy, not affected by water and is of high durability over years, and so in the transferred message.

5 The transfer can be effected a number of times using a single luminescent transfer paper thus enabling it also bo be re-used just as a carbon paper.

6 Several phosphor-radiation systems could be pressed into service with great facilitity depending on the particular application.

7 The special luminescent transfer paper resulting from this invention has the prospects of many other applications.

WE CLAIM:

1. A method for making luminescent transfer paper for preparing invisible copies of the writing which comprises coating a paper sheet with successive layers of grease, wax, a luminescent substance which is substantially invisible in ordinary light, drying the paper after each coating operation, subjecting the same to a mild pressure to stabilise the coating using a roller and giving a final coating of grease.

2 The method as claimed in claim 1 wherein the paper after being coated with the layer of the luminescent substance is further coated with a layer of wax to enhance its protective character.

3 The method as claimed in claim 2, wherein the further coating of the treated paper may be with a mixture of wax and grease layer.

4 The method as claimed in any of the claims 1-3, wherein the coating of the paper is done by spray coating.

5 The method as claimed in claims 1-4 wherein the luminescent substance used may be phosphor zinc sulphide: copper-green, zinc sulphide: silver, blue phosphor $CaWO_4$ blue phosphor, 3.5 MgO, 0.50 MgF_2-GeO_2: Mn red phosphor or $Ca_5(PO_4)_2$, $Ca(Cl,F)_2$:Sb, Mn daylight phosphor excitable by ultraviolet radiation of 2537°A or 3650°A.

6 The method as claimed in claims 1-3 wherein the used is preferably paraffin wax or carnauba wax.

7 The method as claimed in claims 1-4 wherein for coating the paper there are used I. a solution of 0.2 gms of silicone grease in 100 cc of xylene, II. a saturated solution of paraffin wax in benzene, III. a suspension of 5 grams of the luminescent substance in 100 cc of ethyl alcohol with addition of a few drops of acetic acid.

8 The method as claimed in claim 3 and 7 wherein the coating solution II comprises of a mixture of 50:50 of grease of xylene and wax in benzene (solution II A).

9 The method as claimed in claim 1 and 5 wherein the phosphor, luminescent substance used has a particle size in the range of 5 to 50 microns.

10 The method as claimed in any of the preceding claims wherein the coating sequence is: coating with solution I, solution II, suspension III, solution II A and followed by solution I.

Dated this 31st day of July, 1976.

Sd/-
PATENTS OFFICER
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.