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Thermally - sensitive record material.

A thermally-sensitive record material with improved thermal response for a given total coatweight of thermally-sensitive composition or image-forming components has the thermally-sensitive composition applied separately in two or more adjacent layers, each of which contains colour developing coreactant material, rather than in the conventional single layer. The adjacent thermally-sensitive layers are formulated such that together they generate a substantially single colour final print in response to heat energy input. The colour developing coreactant materials in the layers may be the same or different and are typically bisphenols. The colour former is typically a fluoran leucodye.

This invention relates to thermally-sensitive record material.

Thermally-sensitive record material is widely used in facsimile (telecopier) machines, labels, tickets, charts for recording the output of medical or scientific monitoring equipment and for the output of calculators, adding machines, small computer printers and suchlike. In its most common form, the record material comprises a support carrying a coating of a thermally sensitive composition of which the image-forming components are one or more initially colourless or light-coloured electron-donating chromogenic materials (or colour formers) and one or more electron-accepting coreactants (or colour developers) capable of reacting with the chromogenic material to develop its colour. The electron-donating chromogenic material is normally a fluoran or other leucodye and the electron-accepting coreactant is normally an organic acid, most commonly a bisphenol.

The chromogenic material and the coreactant are normally each present in finely-divided particulate form and are dispersed in a suitable matrix material, for example polyvinyl alcohol, which also serves as a binder. The thermally-sensitive composition usually also contains a variety of other ingredients such as sensitizers or modifiers for enhancing the thermal response of the composition, fillers or pigments, lubricants, whiteners, image-stabilizers, and wetting aids.

The support is normally of paper, although plastic film is used for certain products, such as transparencies. The support can if desired be precoated, for example with a pigment/binder composition, and may also carry a back coat on its surface opposite that which carries the thermally-sensitive composition. The thermally-sensitive composition may itself carry a protective topcoat.

In their initial solid state, the chromogenic material and the coreactant do not react together. On selective imagewise application of heat by means of a thermal printer or stylus, local melting of one or more of the components of the thermally-sensitive composition occurs. The liquid phase thus created facilitates reaction between the chromogenic material and the coreactant, thereby developing the colour of the chromogenic material in a pattern corresponding to that of the heat energy input, and so producing an image.

All of the foregoing is very well known and is the subject of an extensive patent literature, and so needs no further description.

An ever-present objective in the art is to improve the thermal response of the record material so as to achieve improved image intensity for a given energy input and/or quantity of colour precursors or a given image intensity for a lower energy input and/or quantity of colour precursors, or some combination of these benefits.

We have now found that improved thermal response is obtained, for a given total coatweight of thermally-sensitive composition or image-forming components, if the thermally-sensitive composition is applied separately in two or more adjacent layers, each of which contains coreactant material, rather than in a single layer. In contrast to previous proposals for multi-colour thermally-sensitive record materials where different layers are used to produce the different colours in response to different levels of imaging heat energy input, often with a decolourizing layer separating the thermally-sensitive layers, the adjacent thermally sensitive layers of the present invention together generate a substantially single colour final print in response to heat energy input.

British Patent Application No. 2110399A discloses a single colour thermally-sensitive record material in which the chromogenic material and the coreactant material are present in separate adjacent layers. The present invention is distinguished from this proposal by the presence of coreactant material in each of the layers making up the thermally-sensitive composition. We have found that this is necessary for the achievement of the desired technical benefits.

Accordingly, the present invention provides in a first aspect a thermally-sensitive record material comprising a support and a thermally-sensitive composition coated on the support, the thermally-sensitive composition including as image-forming components electron-donating chromogenic material and complementary electron-accepting coreactant material effective to develop the colour of the chromogenic material when heat is applied to the composition, characterized in that the thermally-sensitive composition has been applied to the support in the form of a plurality of adjacent layers each of which contains electron-accepting coreactant material and at least one of which also contains electron-donating chromogenic material, and which are formulated such as together to generate a substantially single colour final print in response to a single level of imaging heat energy input.

In a second aspect, the present invention provides a process for the production of thermally-sensitive record material by coating a support with a thermally-sensitive composition, the thermally-sensitive composition including as image-forming components electron-donating chromogenic material and complementary electron-accepting coreactant material effective to develop the colour of the chromogenic material when heat is applied to the composition, characterized in that the thermally-sensitive composition is applied to the support in a plurality of adjacent layers, each of which contains electron-accepting coreactant material and at least one of which also contains electron-donating chromogenic material, and which are formulated such as together to generate a substantially single colour final print in response to a single level of imaging heat energy input.

Whereas it has been conventional to apply a single thermally-sensitive coating at a coatweight in the range 4 to 8 g m⁻², the present invention could for example apply two coatings each of approximately half this coatweight, or less than this if it is desired to take the benefit of the invention wholly or partly as raw material savings rather than all as improved image intensity. It is not however essential that each coating layer should have

5 approximately the same coatweight.

The thermally-sensitive layers may each be of the same or different composition. The latter arrangement can be advantageous in certain circumstances. For example, if two known coreactants are used together in a single thermally-sensitive composition, better image stability can often be obtained than if either of them is used alone (in comparable quantity). However this advantage is counterbalanced by undesired general background colouration of the coating after calendering. If on the other hand the two coreactants are present in

10 different layers, at least one of which also contains chromogenic material, improved thermal image stability can be obtained without such extensive background discolouration. An example of a specific combination of coreactants giving this benefit is that of 2,2-bis (4-hydroxyphenyl)-propane (Bisphenol A) and 2,2-bis (4-hydroxyphenyl)-4-methylpentane when used with a 2,6-diamino-substituted fluoran chromogenic material such

15 as 3-diethylamino-6-methyl-7-anilino-fluoran.

Although the present invention requires the thermally-sensitive composition to be applied in a plurality of layers, there is not necessarily a clear and distinct interface between the layers in the final product. The distinction between the layers is likely to be particularly unclear when each layer is of the same composition.

Although adjacent layers of thermally-sensitive composition are formulated such as together to generate

20 a substantially single colour final print in response to a single level of imaging heat energy input, this is not to say that each layer necessarily produces the same colour, merely that the final print will be a single colour derived from the two layers. Thus if one layer contained a chromogenic material producing a blue print and the other contained a chromogenic material producing a black print, the final substantially single colour print might be blue-black. More usually however, the two layers will each be designed to produce prints of similar hue,

25 either by the use of the same chromogenic materials or chromogenic materials giving similar though not necessarily identical hues.

The present invention can however be employed in a multicolour product, but in this case each distinct print colour will itself be derived from a respective plurality of adjacent layers as defined herein. Thus there might be a plurality of adjacent layers together producing a single colour red image and another separate plurality of adjacent layers together producing a black or blue image.

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The support used in the present thermally-sensitive record material is typically of paper, but plastics film could be used.

Whatever the nature of the support, it can if desired carry one or more precoat(s) on its surface to which the thermally-sensitive composition is applied. Where the support is of paper, the precoat(s) can serve to improve the hold-out and smoothness of the support prior to the application of the thermal coating. Where the support is of plastics film, the precoat(s) can serve to provide a better bond or key to the film. Additionally, and regardless of the nature of the support, the precoat(s) can serve to improve absorptivity with respect to the subsequently-applied thermal composition, to lessen loss of imaging heat energy by dissipation into and through the support, to reduce sticking of the thermal composition to the printhead, to provide anti-static properties, or for other purposes.

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In the case of a paper support at least, the precoat typically comprises one or more pigments and a binder. The pigment(s) may be inorganic or organic, one or more of calcium carbonate, delaminated kaolin or calcined kaolin being preferred.

Each layer of thermally-sensitive composition can be of a conventional nature, as described above. Typical chromogenic compounds for use in the composition(s) are fluorans, particularly derivatives of 2,6-diamino substituted fluorans, and phthalides, particularly, 3,3-bis (4'-dimethylamino-phenyl)-6-dimethylaminophthalide (Crystal Violet Lactone). Specific examples of commercially available fluorans which can be used are 3-diethylamino-6-methyl-7-anilino-fluoran (hereafter referred to by its usual short name of N-102), 3-dibutylamino-6-methyl-7-anilino-fluoran, and 3-N-ethyl-N-isopentylamino-6-methyl-7-anilino-fluoran. Other possible chromogenic materials are those disclosed in our European Patent Application no. 343014A.

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Typical coreactants for use in the composition(s) are bisphenols such as 2,2-bis(4-hydroxyphenyl)-propane (Bisphenol A) and 2,2-bis (4-hydroxyphenyl)-4-methylpentane (hereafter referred to by its usual short name of AP-5), bisphenol sulphones such as bis (4-hydroxyphenyl) sulphone (Bisphenol S), aromatic carboxylic esters such as benzyl 4-hydroxybenzoate, and other coreactants conventional in the art, for example those disclosed in European Patent Application no. 306344A.

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Sensitizers suitable for use in the thermally-sensitive composition(s) are diaryl ethers such as diphenoxyethane, aryl or alkyl substituted biphenyls such as parabenzylbiphenyl, acetoacetic anilides or toluidides, phenylhydroxynaphthoates, and aromatic diesters such as dimethyl or dibenzyl terephthalate and dibenzyl ox-

alate. These materials may be used together with modifiers such as stearamide waxes which also enhance the sensitivity of the thermal composition.

The binder used in the thermally-sensitive composition is typically a polyvinyl alcohol, optionally with starch and/or styrene-butadiene latex or other co-binders and carboxymethyl cellulose or other adjuncts.

Fillers or pigments which may be used in the thermally-sensitive composition(s) are clays, for example delaminated or calcined kaolin, aluminium hydroxide, aluminium oxide, calcium carbonate, talc and zinc oxide. Such materials serve as extenders and whiteners/opacifiers, and, particularly when they have good oil absorption, reduce smudging of the thermal image and build up of the coating on the thermal printing head in use.

The thermally-sensitive composition(s) may also contain optical brighteners, lubricants such as fatty acid salts, for example zinc stearate, to prevent sticking of the composition to the thermal printing head in use, and paraffin wax, which reduces any tendency of the chromogenic material to colour up prematurely and thus improves background whiteness.

The thermally sensitive composition(s) are made up as conventional in the art. Thus, typically the coreactant and the chromogenic material will be separately dispersed in aqueous solutions or emulsions of the binder and bead milled to a particle size in the range 1 to 10 μm e.g. about 2 μm . These separate dispersions will then usually be held for a period of several hours before being mixed. Sensitizer, if used, is generally included in the chromogenic material mixture or the coreactant material mixture, or both, prior to bead milling. The pigment is usually dispersed in water, which may include some binder, before use. The dispersed pigment, together with paraffin wax, if used, and any other ingredients are mixed with the dispersions of the chromogenic material and the coreactant to give the final thermally-sensitive composition for coating on to the support.

The layers of thermally-sensitive composition are conveniently applied to the support in a single pass through a coater equipped with two or more coating stations and a corresponding number of drying stations. Alternatively, each layer can be applied in a separate pass through a single coating station. The coating technique used can be any of those conventional in the art, for example, blade coating, air-knife coating or bar or rod coating, for example Meyer bar coating. After the final coating has been applied, the product may be calendered or supercalendered in conventional manner.

The use of a plurality of layers of thermally-sensitive composition means that each layer has a lower coatweight than a conventional single thermally-sensitive coating. Typically, two 3 g m⁻² coatings might be applied rather than one 6 gm⁻² coating. Since a lower coatweight is being applied, a higher blade pressure may be employed, and this has the advantage of providing an improved coating profile, i.e. a more even coating across and along the web forming the support.

The invention will now be illustrated by the following examples, in which all parts or percentages are by dry weight unless otherwise stated.

Example 1

This illustrates the use of a single thermally-sensitive composition applied in two adjacent layers.

The composition was made up by the following procedure:

1) 19 parts of polyvinyl alcohol were bead milled with 81 parts of 3-N-ethyl-N-isopentylamino-6-methyl-7-anilino fluoran chromogenic material in a 38% solids content aqueous dispersion also containing conventional minor amounts of surfactant.

2) In a separate procedure, 14 parts of polyvinyl alcohol, 18 parts stearamide wax, 25 parts of aluminium hydroxide filler, 31 parts of Bisphenol A and 11 parts of zinc stearate were bead milled in a 42% aqueous dispersion also containing conventional minor amounts of surfactant and defoamer.

3) The milled dispersions from (1) and (2) above were mixed with each other and with an aqueous calcium carbonate dispersion, and additional polyvinyl alcohol, and a minor amount of paraffin wax and cross linker were added to form a thermally-sensitive composition of which the percentage dry composition was as follows:

Chromogenic material	7
Polyvinyl alcohol	15
Coreactant (Bisphenol A)	14
Calcium carbonate	34
aluminum hydroxide	12
Stearamide wax	9
Zinc stearate	5
Other ingredients (as mentioned above)	4
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Some of this composition was applied to conventional precoated thermal base paper by means of a pilot-scale blade coater at an approximate dry coatweight of 3 g m^{-2} . After drying, the paper was put through the coater again to apply a second coating of the thermally-sensitive composition at a dry coatweight of approximately 3 g m^{-2} to give a total dry coatweight of thermally-sensitive composition of approximately 6 gm^{-2} .

Some of the remainder of the thermally-sensitive composition was then applied to the same type of base paper by means of the same pilot blade coater but at an approximate coatweight of 6 gm^{-2} , so as to provide a control paper.

The paper according to the invention and the control paper were then each tested using a thermal print head for which the duration of the input energy pulse could be varied. The intensity of imaging for each input pulse was then determined by means of a Macbeth Densitometer. The processing software of this instrument was arranged to print out the results directly in graphical form, as shown in Fig. 1 attached. This depicts the intensities achieved for each paper at predetermined pulse durations.

It will be seen that at all input energy pulse durations above a lower threshold of about 0.6 milliseconds (ms), the image intensity was always lower for the control paper than for the paper according to the invention. In the very low pulse duration region (c. 0.6 ms and below), virtually no imaging occurred for either paper and comparison is therefore unreliable.

It will be appreciated that although the pulse duration was varied so as to apply different levels of heat energy input for test purposes, the individual prints produced were in response to a single level of imaging heat energy input. The use of different levels of heat energy input in these tests is therefore not in any way analogous to the use of different levels of heat energy input to produce separate images of different colours, as has been proposed in the case of multi-colour thermally-sensitive record materials.

Example 2

This illustrates the use of a system in which different coreactant materials are used in the layers making up the coating of thermally-sensitive composition and in which chromogenic material is present in only one of the layers.

The two coreactant materials were Bisphenol A and AP-5. The chromogenic material was N-102.

In Variant A, 9 parts of polyvinyl alcohol and 91 parts of Bisphenol A were bead milled in aqueous dispersion and applied to precoated thermal base paper by means of a laboratory coater to give an approximate dry coatweight of 3 gm^{-2} . A coating of a composition containing AP-5 and N-102 was then applied over the first coating by means of the same laboratory coater to give an approximate dry coatweight of 4 gm^{-2} . The AP-5/N-102 composition also included p-benzyl biphenyl (pBBP) as sensitizer and other conventional ingredients and was made up by a procedure analogous to that described for the thermally-sensitive composition of Example 1. Its percentage dry composition was as follows:

N-102	6
Polyvinyl alcohol	11
AP-5	13
pBBP	12
Calcium carbonate	33
Silica	10
Stearamide wax	10
Zinc stearate	2
Other ingredients (as in Example 1)	3

In Variant B, the same compositions were used as in Variant A, but the order in which they were coated on the base paper was reversed. The approximate coatweights applied remained the same.

Three control papers were also prepared. In the first of these (Control A), the Bisphenol A and AP-5/N-102 compositions were mixed and applied as a single coating of approximate coatweight 7 g m^{-2} which contained the same ingredients in the same amounts as were present in the two layers applied in Variants A and B. In the second control (Control B), AP-5 was omitted from the N-102 composition and was instead incorporated in the Bisphenol A composition. The resulting Bisphenol A/AP-5 composition was then applied as the first coating and the N-102 composition as the second coating. In the third control (Control C), a single composition was applied as in Control A, except that Bisphenol A was omitted and replaced by a corresponding amount of extra AP-5.

The various papers were each imaged by means of a thermal print head which applied the same level of heat energy input. The image intensity and the background whiteness of an unimaged region were measured using a Macbeth Densitometer.

The results are shown in Table 1 below:

Table 1

Sample	Image Intensity	Background Whiteness
Variant A	1.27	0.08
Variant B	1.25	0.08
Control A	1.12	0.10
Control B	0.90	0.07
Control C	1.05	0.07

It will be seen that Variants A and B both gave significantly improved image intensity compared with a comparable single layer composition (Control A) and this property was even more improved compared with the other controls. The background whiteness of Variants A and B was also better than that of Control A, though not better than those of Controls B and C.

It is also of interest to note that the use of both Bisphenol A and AP-5 as coreactants in a single layer also containing N-102 chromogenic material (Control A) gave better image intensity and background whiteness results than if only one coreactant was used (Control C). However, the background whiteness for Control A was significantly worse than for all other samples. If both coreactants were present in one layer and the chromogenic material was in another layer (Control B), the image intensity was significantly reduced, although the background whiteness was improved.

Example 3

This illustrates the use of the invention to achieve coatweight savings, i. e. reduced raw materials usage whilst maintaining substantially the same image intensity.

A thermally-sensitive composition was made up by:

(1) separately bead milling aqueous dispersions of:

(a) chromogenic material(di-n-butylamino-6-methyl-7-anilino fluoran), sensitizer (p-benzyl-biphenyl, usually known as p-BBP) and polyvinyl alcohol;

(b) coreactant (Bisphenol A), sensitizer (p-BBP) zinc stearate and polyvinyl alcohol;

(c) silica, paraffin wax and stearamide wax; and

(2) mixing the bead milled dispersions so obtained, in the presence of additional polyvinyl alcohol and water.

Single- and two-layer coatings of the composition were then applied to respective sheets of conventional pigment-precoated thermal base paper, the amount of coating applied being such that the single- and double coated sheets gave the same measured image intensity when imaged by means of the same facsimile machine. The coating layers were all applied by means of a laboratory Meyer bar coater, with different Meyer bars being used to achieve different coatweights. The layers of the two-layer coating were each of approximately the same coatweight.

The coatweight of the single-layer coating and the total coatweight of the two-layer coating were then measured. The single-layer coatweight was found to be 4.8 g m^{-2} , but the two-layer total coatweight was only 4.3 g m^{-2} , so demonstrating reduced raw materials usage for the same image intensity.

Example 4

This was similar to Example 3, except that the coreactant was AP-5 and the sensitizer in the coreactant mixture was dibenzyl oxalate (DBO).

The single-layer coatweight was found to be 4.4 g m^{-2} and the two-layer total coatweight 4.2 g m^{-2} , again demonstrating a saving in raw materials usage.

Example 5

This was also similar to Example 3, except that the sensitizer in both the chromogenic material mixture and the coreactant mixture was 1,2 diphenoxy ethane (DPE), the coreactant was AP-5 and the chromogenic material was a mixture of N-102 and 3-N-ethyl-N-isopentylamino-6-methyl-7-anilino fluoran.

The single-layer coatweight was found to be 4.4 g m^{-2} and the two-layer coatweight 4.0 g m^{-2} , again demonstrating a saving in raw materials usage.

Example 6

This illustrates the use of the invention with a thermally-sensitive composition utilizing 4-hydroxy-4'-isopropoxy-diphenyl sulphone (D8) as the coreactant.

The thermally-sensitive composition was made up in a manner similar to that of Example 1 except that D8 replaced Bisphenol A on a weight for weight basis, and the solids content of the initial chromogenic material mixture was slightly lower.

The subsequent procedure was as described in Example 3. The single-layer coatweight was found to be 3.8 g m^{-2} and the two-layer total coatweight 3.2 g m^{-2} , again demonstrating a saving in raw materials usage.

Claims

1. Thermally-sensitive record material comprising a support and a thermally-sensitive composition coated on the support, the thermally-sensitive composition including as image-forming components electron-donating chromogenic material and complementary electron-accepting coreactant material effective to develop the colour of the chromogenic material when heat is applied to the composition, characterized in that the thermally-sensitive composition has been applied to the support in the form of a plurality of adjacent layers each of which contains electron-accepting coreactant material and at least one of which also contains electron-donating chromogenic material, and which are formulated such as together to generate a substantially single colour final print in response to a single level of imaging heat energy input.

2. Thermally-sensitive record material as claimed in claim 1, wherein the coreactant materials in the adjacent layers of thermally-sensitive composition are the same.

3. Thermally-sensitive record material as claimed in claim 1, wherein the coreactant materials in the adjacent layers of thermally-sensitive composition are different.
- 5 4. Thermally-sensitive record material as claimed in claim 2 or 3, wherein the or each coreactant material is a bisphenol.
5. Thermally-sensitive record material as claimed in claim 3 and claim 4, wherein one of the coreactant materials is 2,2-bis(4-hydroxyphenyl)-propane and the other is 2,2-bis(4-hydroxyphenyl)-4-methylpentane (AP-5).
- 10 6. A process for the production of thermally-sensitive record material by coating a support with a thermally-sensitive composition, the thermally-sensitive composition including as image-forming components electron-donating chromogenic material and complementary electron-accepting coreactant material effective to develop the colour of the chromogenic material when heat is applied to the composition, characterized in that the thermally-sensitive composition is applied to the support in a plurality of adjacent
15 layers, each of which contains electron-accepting coreactant material and at least one of which also contains electron-donating chromogenic material, and which are formulated such as together to generate a substantially single colour final print in response to a single level of imaging heat energy input.
- 20 7. A process as claimed in claim 6, wherein the coreactant materials in the adjacent layers of thermally-sensitive composition are the same.
8. A process as claimed in claim 6, wherein the coreactant materials in the adjacent layers of thermally-sensitive composition are different.
- 25 9. A process as claimed in claim 7 or 8, wherein the or each coreactant material is a bisphenol.
10. A process as claimed in claim 8 and claim 9, wherein one of the coreactant materials is 2,2-bis(4-hydroxyphenyl)-propane (Bisphenol A) and the other is 2,2-bis(4-hydroxyphenyl)-4-methylpentane (AP-5).

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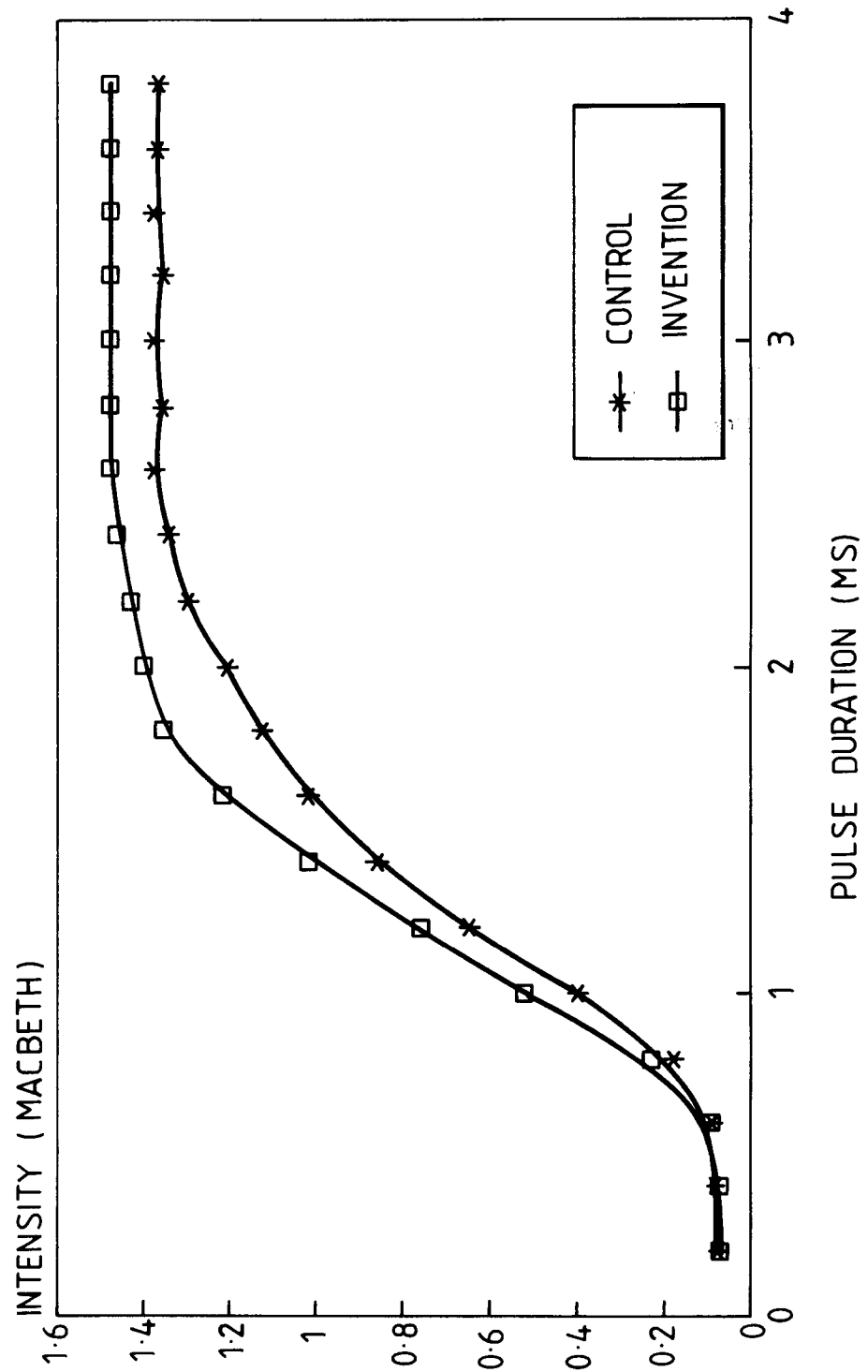
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FIG. 1





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 31 1305

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,D	GB-A-2 110 399 (DAI NIPPON INSATSU KABUSHIKI KAISHA) * page 2, line 28 - line 31; figures 1,2 * * page 3, line 30 - line 45 * ---	1-10	B41M5/30
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 149 (M-694)(2996) 10 May 1988 & JP-A-62 268 684 (HODOGAYA CHEMICALS K.K.) 21 November 1987 * abstract * ---	1-10	
X	PATENT ABSTRACTS OF JAPAN vol. 10, no. 378 (M-546)(2435) 17 December 1986 & JP-A-61 171 383 (FUJI PHOTO FILM COMPANY LIMITED) 2 August 1986 * abstract * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 FEBRUARY 1993	Examiner BACON A.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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