⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: 0 377 961
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 89312472.7

㉒ Date of filing: 30.11.89

(51) Int. Cl.⁵: G03C 1/83, G03C 5/16

㉚ Priority: 23.12.88 GB 8830168

㊸ Date of publication of application:
18.07.90 Bulletin 90/29

(84) Designated Contracting States:
DE FR GB IT

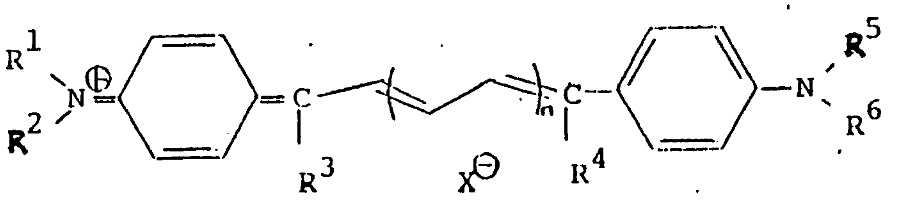
㉑ Applicant: MINNESOTA MINING AND
MANUFACTURING COMPANY
3M Center
Saint Paul, Minnesota 50101(US)

(72) Inventor: Kitchin, Jonathan Peter
4 Valeside
Hertford Herts.(GB)
Inventor: Grzeskowiak, Nicholas Eugenusz
52 Broadway Avenue
Harlow Essex(GB)
Inventor: Helland, Randall Herman
385 Mary Street
Maplewood Minnesota 55119(US)

(74) Representative: Bowman, Paul Alan et al
LLOYD WISE, TREGEAR & CO. Norman
House 105-109 Strand
London WC2R OAE(GB)

(54) Infrared-sensitive photographic materials incorporating antihalation and/or acutance dye.

(57) Photographic materials of the conventional wet processed type or dry silver type, which may be infrared sensitive, containing as an acutance or antihalation dye a compound having a nucleus of the general formula:]



.(I)

in which: n is 1 or 2
R^1, R^2, R^5 and R^6 are independently selected from hydrogen, an alkyl group of up to 30 carbon atoms, an aryl group of up to 10 carbon atoms and an aralkyl group of up to 10 carbon atoms, the necessary atoms to complete a ring fused to the phenyl group to which the nitrogen atom is attached, or R^1 and R^2 together and/or R^5 and R^6 together may represent the necessary atoms to complete a 5- or 6- membered heterocyclic ring which may possess substituents or a fused carbocyclic ring,
R^3 and R^4 are independently selected from hydrogen,a tertiary amino group, an alkyl group of up to 10 carbon atoms, an aryl group of up to 10 carbon atoms or an aralkyl group of up to 10 carbon atoms, or a heterocyclic group of up to 6 atoms selected from C, N, 0 and S, and,
X⊖ represents an anion.

INFRARED-SENSITIVE PHOTOGRAPHIC MATERIALS INCORPORATING ANTIHALATION AND/OR ACUTANCE DYE

This invention relates to a photographic element incorporating an antihalation or acutance dye.

Light sensitive recording materials may suffer from a phenomenon known as halation which causes degradation in the quality of the recorded image. Such degradation may occur when a fraction of the imaging light which strikes the photosensitive layer is not absorbed but passes through to the film base on which the photosensitive layer is coated. A portion of the light reaching the base may be reflected back to strike the photosensitive layer from the underside. Light thus reflected may, in some cases, contribute significantly to the total exposure of the photosensitive layer. Any particulate matter in the photosensitive element may cause light passing through the element to be scattered. Scattered light which is reflected from the film base will, on its second passage through the photosensitive layer, cause exposure over an area adjacent to the point of intended exposure. It is this effect which leads to image degradation. Silver halide based photographic materials (including photothermographic materials) are prone to this form of image degradation since the photosensitive layers contain light scattering particles. The effect of light scatter on image quality is well documented and is described, for example, in T.H. James "The Theory of the Photographic Process", 4th Edition, Chapter 20, Macmillan 1977.

It is common practice to minimise the effects of light scatter by including a light absorbing layer within the photographic element. To be effective the absorption of this layer must be at the same wavelengths as the sensitivity of the photosensitive layer. In the case of imaging materials coated on transparent base, a light absorbing layer is frequently coated on the reverse side of the base from the photosensitive layer. Such a coating, known as an "antihalation layer", effectively reduces reflection of any light which has passed through the photosensitive layer.

A similar effect may be achieved by a light absorbing layer interposed between the photosensitive layer and the base. This construction, described as an "antihalation underlayer" is applicable to photosensitive coatings on transparent or non-transparent bases. A light absorbing substance may be incorporated into the photosensitive layer itself, in order to absorb scattered light. Substances used for this purpose are known as "acutance dyes". It is also possible to improve image quality by coating a light absorbing layer above the photosensitive layer of a photographic element. Coatings of this kind described in U.S. Patent Specifications Nos. 4,312,941, 4,581,323 and 4,581,325, reduce multiple reflections of scattered light between the internal surfaces of a photographic element.

Many substances are known which absorb visible and/or ultraviolet light, and many are suitable for image improvement purposes in conventional photographic elements sensitised to wavelengths below 700 nm. Triarylmethane and oxonol dyes in particular, are used extensively in this connection. There is, however, a need for antihalation and acutance dyes which absorb in the near infrared region of the spectrum.

The use of semiconductor light sources for output of electronically stored image data onto photographic film or paper is becoming increasingly widespread. Since the output of these light sources is usually in the far red or near infrared region of the spectrum there is an increasing demand for high quality imaging materials designed for exposure in this region. This includes conventional wet processed silver halide photographic material and dry, thermally processed materials such as 'dry silver' film and papers.

The classes of organic dyes which are commonly employed for antihalation and/or acutance purposes in ultraviolet and visible light sensitive materials do not readily form stable derivatives which absorb strongly in the near infrared. References to visible light herein refer to wavelengths between 400 and 700 nm and references to near infrared light refer to wavelengths between 700 and 1400 nm, especially 750 to 1300 nm.

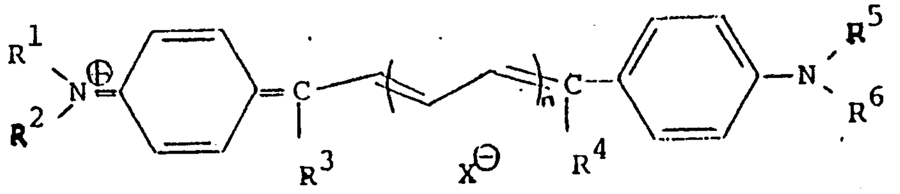
Coatings of antihalation or acutance dyes which absorb in the visible region of the spectrum are usually required to become colourless during processing of the photographic material, either by washing out or chemical reaction in wet processing techniques or thermal bleaching during heat processing techniques.

Since the human eye is insensitive to near infrared radiation, coatings of dyes which absorb only at wavelengths longer than 700 nm appear colourless and would therefore be acceptable in photographic materials without any change in absorption during processing. Dyes of this type would be suitable as antihalation and acutance dyes in infrared sensitive photographic elements. Heptamethine and longer chain cyanine dyes are known which have absorption maxima in the near infrared region of the spectrum. However, simple near infrared absorbing cyanine dyes exhibit an absorption curve which is broadened on the short wavelength side and extends well into the visible region of the spectrum (see for example, A. Weissberger and E.C. Taylor, Special Topics in Heterocyclic Chemistry, John Wiley and Sons, 1977, page 504). This extended absorption curve into the visible results in an objectionably high blue or green appearance which does not disappear during photographic processing.

U.S. Patent Specification No. 4,581,325 discloses a group of heptamethine cyanine dyes having a cyclopentene ring in the polymethine chain which are suitable for use as antihalation or acutance dyes in both wet processed and dry silver photographic materials.

It is an object of the invention to provide an alternative class of dyes which are capable of forming coatings which absorb in the near infrared and have a relatively low visible absorption.

According to the present invention there is provided a photographic element comprising one or more silver halide based photosensitive layers on a substrate characterised in that the element comprises, as an acutance or antihalation dye, a compound having a nucleus of the general formula



(I)

in which: n is 1 or 2

R^1, R^2, R^5 and R^6 are independently selected from hydrogen, an alkyl group of up to 30 carbon atoms, an aryl group of up to 10 carbon atoms and an aralkyl group of up to 10 carbon atoms, the necessary atoms to complete a ring fused to the phenyl group to which the nitrogen atom is attached, or R^1 and R^2 together and/or R^5 and R^6 together may represent the necessary atoms to complete a 5- or 6- membered heterocyclic ring which may possess substituents or a fused carbocyclic ring,

R^3 and R^4 are independently selected from hydrogen, tertiary amino, an alkyl group of up to 10 carbon atoms, an aryl group of up to 10 carbon atoms, an aralkyl group of up to 10 carbon atoms, or a heterocyclic group of up to 6 atoms chosen from C, N, 0 and S.

and $X^\ominus$ represents an anion.

As is well understood in this technical area, a large degree of substitution is not only tolerated, but is often advisable. As a means of simplifying the discussion and recitation of these groups, the terms "group" and "moiety" are used to differentiate between chemical species that allow for substitution or which may be substituted. For example, the phrase "alkyl group" is intended to include not only pure hydrocarbon alkyl chains such as methyl, ethyl, cyclo-hexyl, isooctyl, tert-butyl and the like, but also such alkyl chains bearing such conventional substituents in the art such as hydroxyl, alkoxy, phenyl, halo (F, Cl, Br, I), cyano, nitro, etc. The phrase "alkyl moiety" is limited to the inclusion of only pure hydrocarbon alkyl chains such as methyl, ethyl, propyl, cyclohexyl, isooctyl, tert-butyl, and the like.

The polymethine dyes of formula (I) are known and are disclosed, for example, in W.S. Tuemmler and B.S. Wildi J. Amer. Chem. Soc. 1958, 80, 3772, H. Lorenz and R. Wizinger, Helv. Chem. Acta. 1945, 28, 600, U.S. patent Nos. 2,992,938, 2,813,802, 3,099,630, 3,275,442, 3,436,353 and 4,547,444 and Japanese patent No. 56-109358. The dyes have found utility in infrared screening compositions, as photochromic materials, as sensitizers for photoconductors and as infrared absorbers for optical data storage media. There is no indication that the polymethine dyes of formula (I) would have suitable properties for use as antihalation dyes.

The dyes may be incorporated into wet processed photographic or dry processed photothermographic elements as acutance dyes according to conventional techniques. The dyes may also be incorporated into antihalation layers according to techniques of the prior art, for example, as an antihalation backing layer, an antihalation underlayer or as an overcoat.

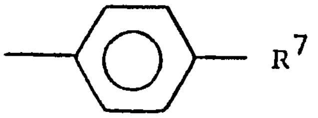
The dye is preferably incorporated into the layer in a quantity which will provide a density of from 0.05 to 2, most preferably 0.1 to 1.0 over the general wavelength range to which the element is sensitised. Dyes of structure (1) are found to have particularly suitable properties for antihalation purposes for the following reasons. In most cases the dyes have a high absorption in the near infrared region and thus provide good antihalation protection. Many of the dyes possess a low absorption in the visible region and hence exhibit a low visible residual stain in photographic applications employing thermal processing. The dyes of structure (1) also unexpectedly undergo bleaching by conventional photographic developer compositions and are therefore suitable for antihalation purposes in conventional wet-processed silver halide photographic materials since in this case even the slight visible residual stain is bleached away by the processing solutions leaving a desirable colourless background.

The photothermographic medium may be selected from any of the known systems, e.g. those disclosed in U.S. Patent Nos. 3,152,904 and 3,457,075. Preferred photothermographic media are dry silver systems comprising a thermally developable mixture of light sensitive silver halide with a silver salt of an organic fatty acid, e.g. behenic acid, and a mild reducing agent. The components of the medium may be coated in one or more layers. The components of the photothermographic medium and the antihalation layer may be maintained in nonreactive association, if necessary by the presence of a barrier layer between the antihalation and imaging layers.

In the dyes of formula (I) R^1, R^2, R^5 and R^6 are preferably alkyl groups, more preferably alkyl moieties of 1 to 5 carbon atoms. Preferably $R^1 = R^2 = R^5 = R^6$. However R^1, R^2, R^5 and R^6 may be selected from a wide range of aryl e.g phenyl, and aralkyl groups as known in the art. The alkyl, aryl and aralkyl groups may possess substituents of the type known in polymethine dyes e.g. halogen, alkoxy, CN, OH, carboxyl etc.

R^1, R^2, R^5, and R^6 may also represent the necessary atoms to complete a ring fused to the phenyl group to which the nitrogen atom is attached. For example R^1 and R^2 may complete a julolidine group.

R^3 and R^4 preferably represent an optionally substituted phenyl group, more preferably:

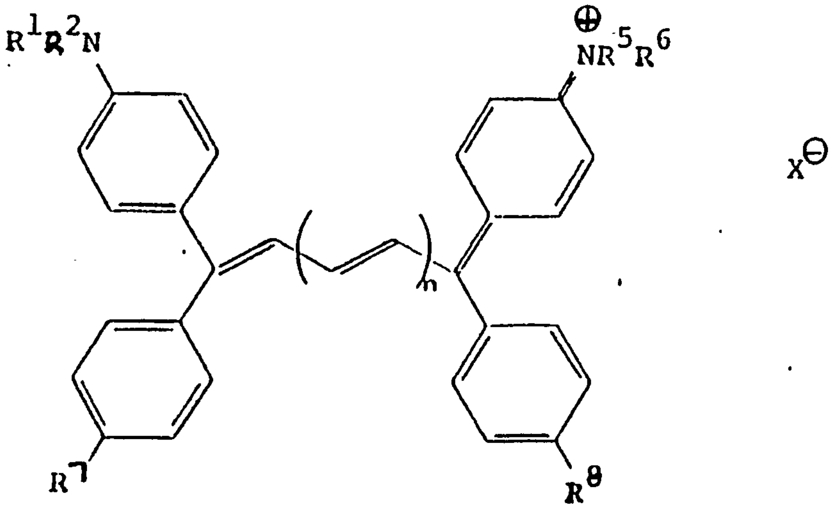


in which R^7 is selected from hydrogen, halogen, hydroxy, alkyl of 1 to 5 carbon atoms, alkoxy of 1 to 5 carbon atoms and $-NR^9R^{10}$ in which R^9 and R^{10} may be the same or different and are selected from the same groups as R^1 and R^2.

$X^\ominus$ may be any suitable anion including halide e.g. Cl,Br; halogen- containing complex anions e.g. tetrafluoroborate, hexafluorophosphate, $RCOO^-$ and RSO^{-3} in which R is alkyl or aryl of up to 20 carbon atoms and which may be fluorinated e.g. CF_3COO^-, $CF_3SO_3^-$.

The polymethine chain and phenyl groups in formula (I) may possess substituents of the type known in the art. The free bonds of the polymethine chain are preferably satisfied by hydrogen. However, substituents may be present on the polymethine chain, e.g. hydroxy, alkyl, alkoxy, aryl and aryloxy groups, which groups may be substituted and generally contain up to 8 carbon atoms. Halogen atoms and CN groups may also be substituted on the polymethine chain. Although chain substituents are not generally preferred, they are well known in the dye art.

A preferred group of compounds of formula (I) are of the formula:



(II)

in which R^1, R^2, R^5, R^6, R^7, n and X are as defined above and R^8 has the same definition as R^7.

Specific examples of compounds of formula (II) are reported in the following Table.

TABLE

Compound No.	$R^1 = R^2$	$R^5 = R^6$	$R^7 = R^8$	n	X^-
1	CH_3	CH_3	H	1	CF_3SO_3
2	CH_3	CH_3	$N(CH_3)_2$	1	CF_3SO_3
3	C_2H_5	C_2H_5	$N(C_2H_5)_2$	1	CF_3SO_3
4	CH_3	CH_3	Cl	1	CF_3SO_3
5	CH_3	CH_3	OCH_3	1	CF_3SO_3
6	CH_3	CH_3	$N(CH_3)_2$	2	CF_3SO_3

The invention will now be illustrated by the following Examples.

EXAMPLE 1

Aqueous 5% gelatin (200g) containing a wetting agent (4.6cm^3 10% Hostapur SAS 93 available from Hoechst) was adjusted to a pH of 4.5 and heated to 65°C. The dye (1) (0.25g) was dissolved in methanol (25cm^3) at 60°C and added to the aqueous gelatin with stirring. The mixture was cooled to 50°C and hardener (8cm^3 2% formaldehyde) was added. The solution was coated on polyethylene terephthalate base at 66cm^3 m^{-2}. The coating exhibited an optical absorption of 0.5 at 815 nm and a pale pink visible colouration. An infrared sensitive silver halide coating was made on the reverse side of the base. The photographic element thus formed was exposed with a resolution test pattern using a laser diode scanning device emitting infrared radiation at 815 nm. The material was processed in an automatic X-ray film processor using Kodak RP X-O mat developer under standard conditions. The processed film exhibited a sharp image on a colourless background.

A similar material prepared without the antihalation backing produced a blurred image under the same test conditions.

EXAMPLE 2

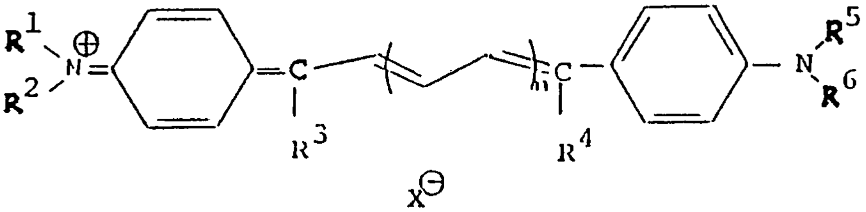
Polymethine dye (1) (0.085g) was dissolved in a mixture of N-methyl pyrrolidone (8.7g) and methanol (6.7g). To this solution was added a solution of cellulose acetate butyrate (6.2g) and PE200 polyester resin (0.8g) in a mixture of toluene (20.9g) and butan-2-one (43g). A solution of methyl isobutyl ketone (7.0g) in methanol (7.0g) was also added. The final solution was coated onto polyethylene terephthalate base at a wet thickness of 60 microns and dried for 4 minutes at 80°C to give an optical density of 0.4 at 780 nm.

A dry silver type photothermographic construction was coated on the reverse side of the base. The photothermographic element thus formed was exposed to a test pattern of near infrared radiation (780 nm). The material was processed by heating to 127°C for six seconds. A sharp image on a faintly coloured magenta background was produced. A similar coating was produced using blue tinted polyester base of the type used for medical X-ray film. In this case no residual stain was observable.

Coatings made for comparison without the antihalation backing produced a blurred image under the same test conditions.

Claims

1. A photographic element comprising one or more silver halide based photosensitive layers on a substrate characterised in that the element comprises, as an acutance or antihalation dye, a compound having a nucleus of the general formula



(I)

in which: n is 1 or 2

R^1, R^2, R^5 and R^6 are independently selected from hydrogen, an alkyl group of up to 30 carbon atoms, an aryl group of up to 10 carbon atoms and an aralkyl group of up to 10 carbon atoms, the necessary atoms to complete a ring fused to the phenyl group to which the nitrogen atom is attached, or R^1 and R^2 together and/or R^5 and R^6 together may represent the necessary atoms to complete a 5- or 6- membered heterocyclic ring which may possess substituents or a fused carbocyclic ring,

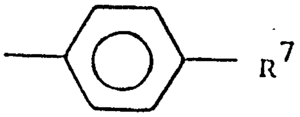
R^3 and R^4 are independently selected from hydrogen,a tertiary amino group, an alkyl group of up to 10 carbon atoms, an aryl group of up to 10 carbon atoms or an aralkyl group of up to 10 carbon atoms, or a heterocyclic group of up to 6 atoms selected from C, N, O and S, and,

$X^{\ominus}$ represents an anion.

2. A photographic element as claimed in Claim 1 in which R^1, R^2, R^5 and R^6 each represent alkyl moieties of from 1 to 5 carbon atoms.

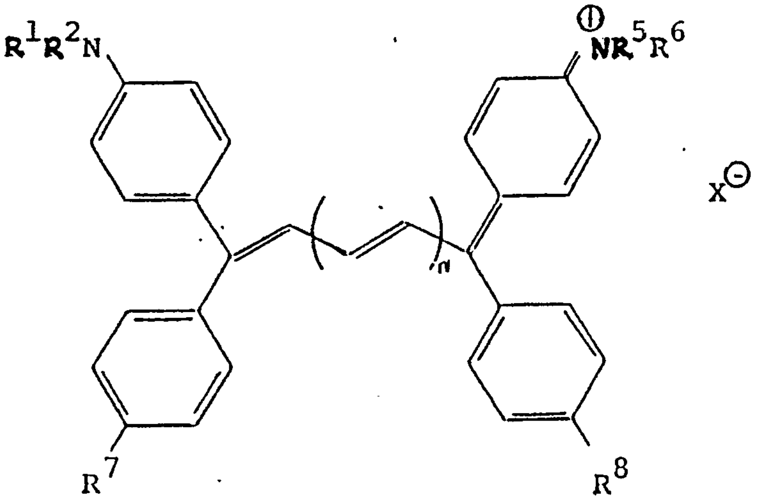
3. A photographic element as claimed in Claim 1 or Claim 2 in which R^3 and R^4 are optionally substituted phenyl groups.

4. A photographic element as claimed in any preceding claim in which R^3 and R^4 are groups of the formula:



in which R^7 represents halogen, an alkyl group of 1 to 5 carbon atoms, an alkoxy group of 1 to 5 carbon atoms or $-NR^9R^{10}$ in which R^9 and R^{10} may be the same or different and have the same definition as R^1 and R^2 in Claim 1.

5. A photographic element as claimed in any preceding claim in which the dye has the formula:



(II)

in which R^1, R^2, R^5, R^6, n and X are as defined in Claim 1 and R^7 and R^8 may be the same or different and represent halogen, an alkyl group of 1 to 5 carbon atoms, an alkoxy group of 1 to 5 carbon atoms or $-NR^9R^{10}$ in which R^9 and R^{10} independently represent a hydrogen atom or an alkyl group of 1 to 5 carbon atoms.

6. A photographic element as claimed in any preceding claim in which the dye is present in a layer to

provide an optical density to the layer of from 0.05 to 2.0.

7. A photographic element as claimed in Claim 6 in which the dye is present in a layer to provide an optical density to the layer of from 0.1 to 1.0.

8. A photographic element as claimed in any preceding claim in which the photographic element is a conventional wet processed photographic element.

9. A photographic element as claimed in any one of Claims 1 to 7 in which the photographic element is a photothermographic element comprising a light sensitive silver halide in association with a silver salt of an organic acid.

10. A photographic element as claimed in any preceding claim in which the dye of formula (I) is present in an antihalation backing on said substrate.

11. A photographic element as claimed in any one of Claims 1 to 9 in which the dye of formula (I) is present as an underlayer between said substrate and said one or more photosensitive layers.

12. A photographic element as claimed in any one of Claims 1 to 9 in which the dye of formula (I) is present in an overcoat above the photosensitive layer.

13. A photographic element as claimed in any one of Claims 1 to 9 in which the dye formula (I) is present in the photosensitive layer.

14. A photographic element as claimed in any preceding claim characterised in that the photosensitive layer are infrared sensitive.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 31 2472

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)
D,Y	US-A-3 275 442 (H. KOSENKRANIUS et al.) * Column 1, line 30 - column 2, line 28; column 2, lines 62-64 *	1-8,10-14	G 03 C 1/83 G 03 C 5/16
D,Y	US-A-4 547 444 (V.L. BELL et al.) * Column 5, lines 18-32 *	1-8,10-14	
Y	EP-A-0 264 788 (KONSHIROKU PHOTO INDUSTRY CO. LTD) * Page 20, lines 44-50; page 22, structure D and line 31 *	1-8,10-14	
A	US-A-3 652 288 (A. FUMIA et al.) * Column 1, lines 45-47; claim 1, structure 3 *	1-14	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C 1/00
G 03 C 5/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-04-1990	BOLGER W.

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