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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: INFRARED RAY-ABSORBING FIBERS

(57) Abstract: The invention relates to the use of polyamide fibres, polyester fibres, cellulose fibres or mixed fibres containing polyamide fibres, polyester fibres or cellulose fibres dyed or printed with a specific phthalocyanine dye for the production of camouflage equipment.

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- 1 -

Infrared Ray-absorbing Fibers

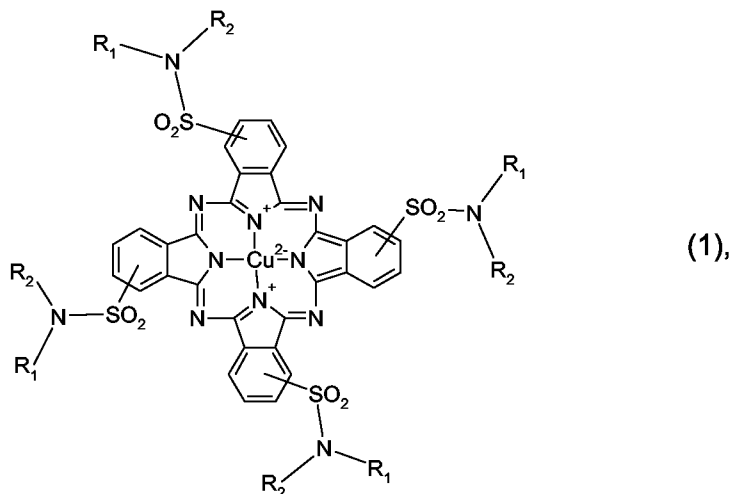
The invention relates to the use of fibres dyed or printed with a specific phthalocyanine dye for the production of camouflage equipment.

- 5 The purpose of camouflage is to adapt clothing and military objects to their natural surroundings. Textile materials for military purpose usually are made of synthetic fibres, like polyester or polyamide, or mixed cellulose/synthetic fibres and are generally dyed in yellowish-beige, medium brown, grey, green or olive-coloured hues.
- With regard to an effective camouflage, it is necessary to defeat infrared imaging systems by
 10 making it difficult for the device to discriminate between the potential target object and its background. In order to avoid contrasts and to break outlines, clothes should exhibit 10-50 % reflectance in 700-1200 nm range, depending on shade.
- Accordingly, there is a need for dyestuffs suitable for dyeing synthetic or mixed
 cellulose/synthetic fibres which, alone or in combination with other dyes, allow combined
 15 visual and infrared camouflage. At the same time, a high fastness level is stipulated, especially with regard to lightfastness and washfastness.

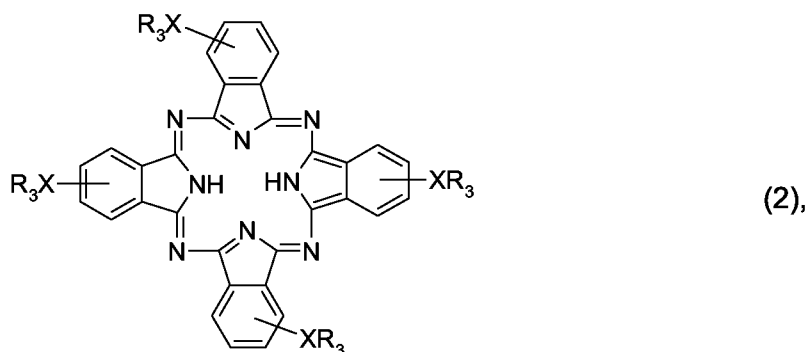
It has now surprisingly been found that certain specific phthalocyanine dyes meet the criteria given above to a considerable degree.

20

The present invention relates to the use of polyamide fibres, polyester fibres, cellulose fibres or mixed fibres containing polyamide fibres, polyester fibres or cellulose fibres dyed or printed with a phthalocyanine dye of formula (1) or (2)



- 2 -



wherein R_1 and R_2 independently of the other denote hydrogen, C_1 - C_{20} alkyl or C_1 - C_{20} alkyl interrupted by one or more oxygen or sulphur atoms,
 5 X represents oxygen or sulphur, and
 R_3 is C_1 - C_{20} alkyl, C_5 - C_{30} aryl or C_6 - C_{36} aralkyl,
 for the production of camouflage equipment.

10 The compounds of formulae (1) and (2) are known and either commercially available or can be prepared according to known processes.

Preferred compounds of formula (1) are those wherein R_1 is hydrogen and R_2 denotes C_1 - C_{12} alkyl or $-(CH_2CH_2O)_n-CH_3$, wherein n is a number from 1 to 5.

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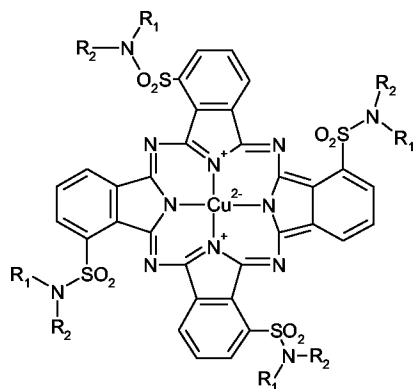
Particularly preferred dyes are the compounds of formula (1), wherein R_1 is hydrogen and R_2 denotes C_1 - C_8 alkyl.

Preferred compounds of formula (2) are those wherein R_3 denotes C_1 - C_{12} alkyl.

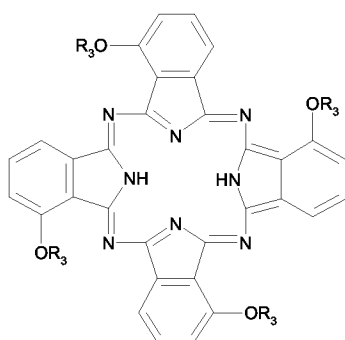
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Especially preferred are the phthalocyanine dyes of formula (1a) and (2a),

- 3 -



(1a),

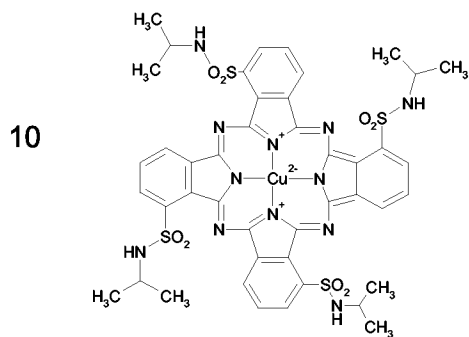


(2a)

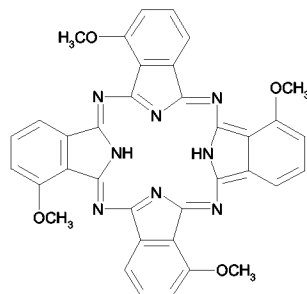
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wherein R_1 , R_2 and R_3 are as defined above.

The most preferred phthalocyanine dyes are the compounds of formula (101) and (102)



(101)



(102).

In order to attain specific hues or colour nuances, the phthalocyanine dyes of formula (1) and (2) can advantageously be combined with other dyes or pigments.

The term "camouflage equipment" includes all articles intended for camouflage purposes, preferably for military purposes, which can be prepared from polyamide fibres, polyester fibres, cellulose fibres or mixed fibres containing any of these fibres.

Such articles may be, for example, clothes, luggage, coverings for hiding vehicles or
5 buildings, parachutes, artificial floors, panelings inside vehicles or buildings etc.

The application of the phthalocyanine dyes of formula (1) or (2) or dye mixtures containing phthalocyanine dyes of formula (1) or (2) to the fibre materials can be effected in accordance with known colouring methods, for example with the thermosol process for dyeing or
10 conventional printing processes.

In such processes, the said fibre materials can be in a variety of processing forms, e.g. in the form of woven or knitted fabrics.

15 It is advantageous to convert the dyes of formula (1) or (2) or dye mixtures containing one of these dyes into a dye preparation prior to use. For this purpose, the dye is ground so that its particle size is on average from 0.1 to 10 microns. Grinding can be carried out in the presence of dispersants. For example, the dried dye is ground together with a dispersant or kneaded into a paste form together with a dispersant. It can be used in liquid form as
20 dispersion or it can be dried *in vacuo* by atomisation. After adding water, the resulting preparations can be used to prepare printing pastes and dyebaths.

For printing, the customary thickeners will be used, e.g. modified or unmodified natural products, for example alginates, British gum, gum arabic, crystal gum, locust bean flour,
25 tragacanth, carboxymethyl cellulose, hydroxyethyl cellulose, starch or synthetic products, for example polyacrylamides, polyacrylic acid or copolymers thereof, or polyvinyl alcohols.

Polyester or polyamide fibre materials can be dyed in the thermosol process from an aqueous dispersion in the presence of customary additives, preferably at temperatures of
30 from 80 to 180°C.

Accordingly, a further object of the invention is the use of polyamide fibres or polyester fibres dyed with a phthalocyanine dye of formula (1) or (2) according to claim 1 in the thermosol

process for the production of camouflage equipment.

Phthalocyanine dyes of formula (1) or (2) are suitable for the mass-colouration of plastics, too.

5 Hence, the colouring of polyesters and polyamides with the phthalocyanine dyes of formula (1) or (2) can be carried out, for example, by mixing such a dye into those substrates using roll mills, mixing apparatus or grinding apparatus, with the result that the dye is dissolved or finely dispersed in the high molecular weight material. The high molecular weight organic material with the admixed dye is then processed using processes known *per*
10 se, for example calendering, compression moulding, extrusion, coating, spinning, casting or injection moulding, whereby the coloured material acquires its final form. It is also possible for the admixing of the dye to be carried out immediately prior to the actual processing step, by continuously feeding a solid dye (for example in powder form) and, at the same time, a granulated or pulverulent high molecular weight organic material, and optionally also
15 additional ingredients, e.g. additives, directly into the intake zone of an extruder, where mixing takes place just before processing. In general, however, it is preferable for the dye to be mixed into the high molecular weight organic material beforehand, because more even colouration of the substrates can be obtained.

20 It is also possible, in order to achieve different shades of colour, to add to the high molecular weight organic materials, in addition to the phthalocyanine dye of formula (1) or (2), also further pigments or other colorants in any desired amounts, optionally together with further additives, e.g. fillers or siccatives.

25 The invention further relates to the use of polyamide fibres or polyester fibres mass-coloured with a phthalocyanine dye of formula (1) or (2) according to claim 1 for the production of camouflage equipment.

A further object of the invention is the use of polyamide fibres, polyester fibres, cellulose
30 fibres or mixed fibres containing polyamide fibres, polyester fibres or cellulose fibres printed with a phthalocyanine dye of formula (1) or (2) as defined above.

Several attempts have been made to develop efficient processes for printing or dyeing mixed cellulose/synthetic fibres, for example polyester-cotton blends.

Two fundamentally different approaches were taken:

Processes using one class of dye only and processes using mixtures of two classes of dyes. Usually reactive dyes or vat dyes are combined with disperse dyes.

- 5 However, the use of such dye mixtures is associated with several drawbacks and it is hardly possible to obtain the same colour and depth on the two fibres by this method.

Processes for dyeing cellulose fibres or blends of cellulose fibres and synthetic fibres with a single disperse dye have also been described. However, the top requirements with respect to light fastness and wash fastness in most cases have not been met.

- 10 Cellulose or mixed cellulose/synthetic fibres can advantageously be dyed with phthalocyanine dyes of formula (1) or (2) or dye mixtures containing phthalocyanine dyes of formula (1) or (2) according to the process described in WO 2005/024123, hereby incorporated by reference.
- 15 The invention therefore further relates to the use of cellulose or mixed cellulose/synthetic fibres which were treated in any sequence with water, a water-soluble organic solvent having a boiling point $>150^{\circ}\text{C}$ and a phthalocyanine dye of formula (1) or (2) as defined in claim 1 for the production of camouflage equipment.
- 20 A further object of the invention is the camouflage equipment prepared by dyeing or printing polyamide fibres, polyester fibres, cellulose fibres or mixed fibres containing polyamide fibres, polyester fibres or cellulose fibres dyed or printed with a phthalocyanine dye of formula (1) or (2) to claim 1.
- 25 The following non-limitative Examples illustrate the invention in more detail.

Application Examples:Example 1

1. Preparation of the Dispersion

5 The dye of formula (101) is dispersed according to the following formulation:

- 29,2% dye
- 7.3% 1,2-propylenglykol (solvent)
- 3.7% Lutensol AT25 (dispersant)
- 0.8% Geropon T77 (wetting agent)
- 10 • 0.1% Surfinol DF58 (antifoam agent)
- 0.4% Proxel GXL (antimicrobial)
- 58.5% deionised water

15 Zirconium beads (diameter 0.6 to 1mm) are then added to the above-obtained dispersion in a glass bottle tightly closed. The bottle is then placed in a Scandex apparatus and thereby agitated for 4 hours. The thus obtained fine dispersion is then filtered on a conventional Büchner funnel to provide the final dye dispersion.

2. Preparation of the Printing paste

20 A typical run consists in the preparation of a mother paste, to which a quantity of the dye dispersion and water will be subsequently added.

- Mother paste:

- 84.2% deionised water
- 25 • 0.8% NH₄OH (28%)
- 0.4% Alcoprint PA-NS
- 9.9% PEG400
- 2.3% Alcoprint PSC
- 2.4% Alcoprint PTP

30

- Printing paste

- 33.3% deionised water
- 60.1% mother paste
- 6.6% dye dispersion

The amount of added deionised water can vary as a function of the viscosity of the dye dispersion and/or of the printing paste.

5 3. Printing

The printing paste is applied in a classical way on the textile (PES/CO 67/33) through a screen. After drying at 90°C, the textile is thermofixed at 220°C for 1 minute.

After a brief cold rinse, a 30 minutes wash at 80°C is performed in a bath containing:

- 2g/L carbonate
- 10 • 1g/L Calgon
- 1g/L Ultravon JU

4. Tests

15 The thus obtained printed fabric exhibits a very good light fastness, wash fastness, fastness to bleaching with hypochlorite (ISO 105-N01) and wet rubbing fastness.

The resulting printed textile has the following IR reflection spectrum:

Wavelength [nm]	Reflectance
650	0.023
700	0.032
750	0.052
800	0.182
850	0.448
900	0.602
950	0.717
100	0.723
1050	0.659
1100	0.666
1150	0.804
1200	0.810

Example 2:

Example 1 is repeated by using the same amount of dye of formula (102) instead of dye of
5 formula (101).

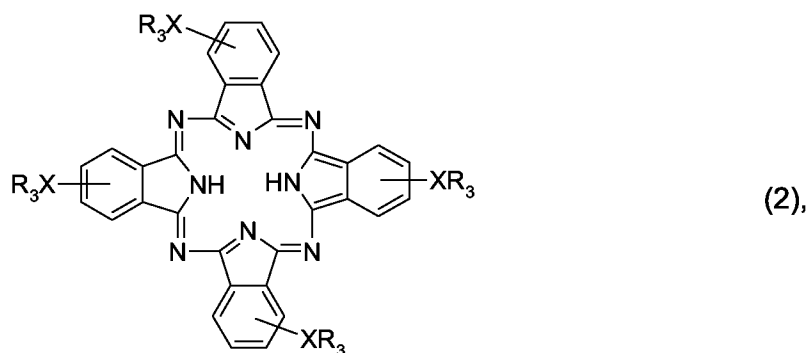
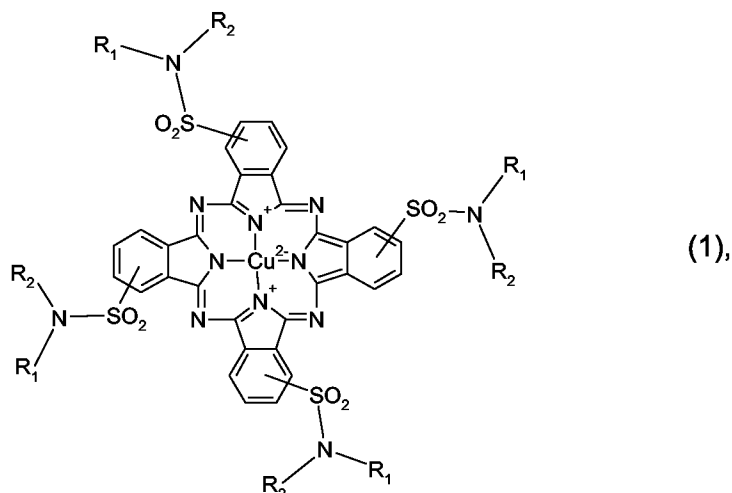
The thus obtained printed fabric exhibits a very good light fastness, wash fastness, fastness
to bleaching with hypochlorite (ISO 105-N01) and wet rubbing fastness.

The resulting printed textile has the following IR reflection spectrum:

Wavelength [nm]	Reflectance
650	0.030
700	0.027
750	0.041
800	0.053
850	0.104
900	0.375
950	0.575
100	0.643
1050	0.677
1100	0.699
1150	0.706
1200	0.715

Claims

1. Use of polyamide fibres, polyester fibres, cellulose fibres or mixed fibres containing
polyamide fibres, polyester fibres or cellulose fibres dyed or printed with a phthalocyanine
dye of formula (1) or (2)



wherein R_1 and R_2 independently of the other denote hydrogen, C_1 - C_{20} alkyl or C_1 - C_{20} alkyl interrupted by one or more oxygen or sulphur atoms,

X represents oxygen or sulphur, and

R_3 is C_1 - C_{20} alkyl, C_5 - C_{30} aryl or C_6 - C_{36} aralkyl,

for the production of camouflage equipment.

2. Use of fibres according to claim 1 dyed or printed with a phthalocyanine dye of formula (1), wherein R_1 is hydrogen and R_2 denotes C_1 - C_{12} alkyl or $-(CH_2CH_2O)_n-CH_3$, wherein n is

- 11 -

a number from 1 to 5.

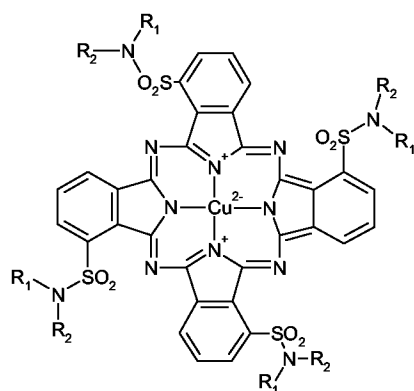
3. Use of fibres according to claim 1 dyed or printed with a phthalocyanine dye of formula (1), wherein R_1 is hydrogen and R_2 denotes C_1 - C_8 alkyl.

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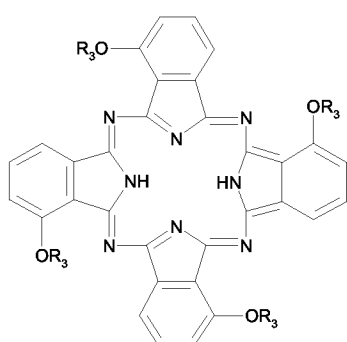
4. Use of fibres according to claim 1 dyed or printed with a phthalocyanine dye of formula (2), wherein R_3 denotes C_1 - C_{12} alkyl.

5. Use of fibres according to claim 1 dyed or printed with a phthalocyanine dye of formula (1a) or (2a),

10



(1a),



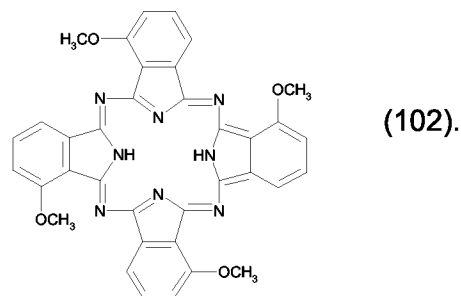
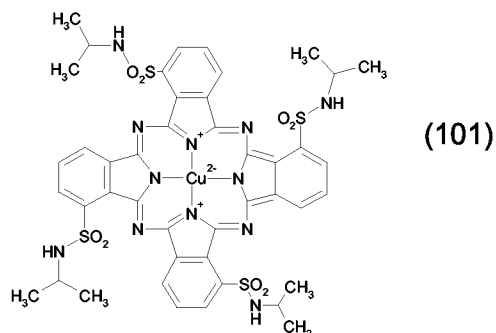
(2a)

15

wherein R_1 , R_2 and R_3 are as defined in claim 1.

6. Use of fibres according to claim 1 dyed or printed with a phthalocyanine dye of formula (101) or (102),

20



7. Use of polyamide fibres or polyester fibres dyed with a phthalocyanine dye of formula (1) or (2) according to claim 1 in the thermosol process for the production of camouflage equipment.
8. Use of polyamide fibres or polyester fibres mass-coloured with a phthalocyanine dye of formula (1) or (2) according to claim 1 for the production of camouflage equipment.
9. Use of polyamide fibres, polyester fibres, cellulose fibres or mixed fibres containing polyamide fibres, polyester fibres or cellulose fibres printed with a phthalocyanine dye of formula (1) or (2) according to claim 1 for the production of camouflage equipment.
10. Use of cellulose or mixed cellulose/synthetic fibres which were treated in any sequence with water, a water-soluble organic solvent having a boiling point >150 °C and a phthalocyanine dye of formula (1) or (2) as defined in claim 1 for the production of camouflage equipment.
11. Camouflage equipment prepared by dyeing or printing polyamide fibres, polyester fibres, cellulose fibres or mixed fibres containing polyamide fibres, polyester fibres or cellulose fibres dyed or printed with a phthalocyanine dye of formula (1) or (2) as defined above.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/064946

A. CLASSIFICATION OF SUBJECT MATTER

INV. D06P1/00 D06P1/26 D06P1/38

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D06P

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 977 740 C (ELTRO G.M.B.H. & CO., GESELLSCHAFT FUER STRAHLUNGSTECHNIK) 27 March 1969 (1969-03-27) page 2, line 3 - line 11; claims	1-11
Y	DE 66 09 396 U (ELTRO GMBH & CO, GESELLSCHAFT FUER STRAHLUNGSTECHNIK) 10 May 1972 (1972-05-10) page 7, paragraph 2; claims	1-11
Y	US 4 095 940 A (WEINGARTEN ET AL) 20 June 1978 (1978-06-20) example 8	1-11
Y	DE 102 04 829 C1 (HUGO, GERD) 17 July 2003 (2003-07-17) page 3, paragraph 18 - paragraph 20; claim 14	1-11
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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- * & * document member of the same patent family

Date of the actual completion of the international search

30 August 2006

Date of mailing of the international search report

06/09/2006

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Koegler-Hoffmann, S

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/064946

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/024123 A (CIBA SPECIALTY CHEMICALS HOLDING INC; HALL-GOULLE, VERONIQUE; TZIKAS,) 17 March 2005 (2005-03-17) cited in the application the whole document -----	11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/064946

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 977740	C	NONE	
DE 6609396	U	10-05-1972	NONE
US 4095940	A	20-06-1978	BE 793350 A1 DE 2200323 C1 15-06-1978 FR 2370821 A1 09-06-1978 GB 1501370 A 15-02-1978 NL 7300160 A 30-12-1977
DE 10204829	C1	17-07-2003	AU 2003206643 A1 02-09-2003 CA 2475474 A1 14-08-2003 CN 1646638 A 27-07-2005 WO 03066746 A1 14-08-2003 EP 1472318 A1 03-11-2004 JP 2005516808 T 09-06-2005 MX PA04007548 A 05-12-2005 NZ 534481 A 27-05-2005 US 2005129964 A1 16-06-2005 ZA 200406240 A 13-06-2005
WO 2005024123	A	17-03-2005	NONE