

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 1 065 049 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**03.01.2001 Bulletin 2001/01**

(51) Int. Cl.<sup>7</sup>: **B41C 1/10**, B41M 5/36

(21) Application number: **00201854.7**

(22) Date of filing: **24.05.2000**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

Designated Extension States:

**AL LT LV MK RO SI**

(30) Priority: **29.06.1999 EP 99202108**

(71) Applicant: **AGFA-GEVAERT N.V.**

**2640 Mortsel (BE)**

(72) Inventors:

- **Vermeersch, Joan,  
Agfa-Gevaert N.V.  
2640 Mortsel (BE)**
- **Van Damme, Marc,  
Agfa-Gevaert N.V.  
2640 Mortsel (BE)**

(54) **Heat-sensitive imaging element with cover layer for providing a lithographic printing plate**

(57) According to the present invention there is provided a heat-sensitive material for making lithographic printing plates comprising on a lithographic support an image-forming layer comprising a hydrophilic binder, a cross-linking agent for a hydrophilic binder and dispersed hydrophobic thermoplastic polymer particles, characterized in that said image-forming layer is covered with a layer comprising at least one organic compound comprising cationic groups.

**EP 1 065 049 A1**

## Description

### FIELD OF THE INVENTION

- 5 [0001] The present invention relates to a heat-sensitive material for preparing lithographic printing plates.  
 [0002] More specifically the invention is related to a processless heat-sensitive material which yields lithographic printing plates with a high lithographic latitude.

### BACKGROUND OF THE INVENTION

- 10 [0003] Lithographic printing is the process of printing from specially prepared surfaces, some areas of which are capable of accepting ink, whereas other areas will not accept ink.  
 [0004] In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy ink in the photo-exposed (negative working) or in the non-exposed areas (positive working) on an ink-repelling background.  
 15 [0005] In the production of common lithographic plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or obtains such affinity by chemical treatment is coated with a thin layer of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophilic colloids and a large variety of synthetic photopolymers. Particularly diazo-sensitized systems are widely used.  
 20 [0006] Upon imagewise exposure of such light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.  
 [0007] On the other hand, methods are known for making printing plates involving the use of imaging elements that are heat-sensitive rather than photosensitive. A particular disadvantage of photosensitive imaging elements such as  
 25 described above for making a printing plate is that they have to be shielded from daylight. Furthermore they have a problem of unstable sensitivity with regard to the storage time and they show a lower resolution. The trend towards heat-sensitive printing plate precursors is clearly seen on the market.  
 [0008] For example, **Research Disclosure no. 33303 of January 1992** discloses a heat-sensitive imaging element comprising on a support a cross-linked hydrophilic layer containing thermoplastic polymer particles and an infrared absorbing pigment such as e.g. carbon black. By image-wise exposure to an infrared laser, the thermoplastic  
 30 polymer particles are image-wise coagulated thereby rendering the surface of the imaging element at these areas ink accepting without any further development. A disadvantage of this method is that the printing plate obtained is easily damaged since the non-printing areas may become ink-accepting when some pressure is applied thereto. Moreover, under critical conditions, the lithographic performance of such a printing plate may be poor and accordingly such printing  
 35 plate has little lithographic printing latitude.  
 [0009] Furthermore **EP-A- 770 494, 770 495, 770 496 and 770 497** disclose a method for making a lithographic printing plate comprising the steps of (1) image-wise exposing to light a heat-sensitive imaging element comprising (i) on a hydrophilic surface of a lithographic base an image-forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder and (ii) a compound capable of converting light to heat, said compound being  
 40 comprised in said image-forming layer or a layer adjacent thereto; (2) and developing a thus obtained image-wise exposed element by rinsing it with plain water.  
 [0010] The above mentioned heat-sensitive imaging elements for making lithographic printing plates are not optimal regarding lithographic latitude, more particularly they need a lot of prints before the background area becomes free of printing ink.

### OBJECTS OF THE INVENTION

- 45 [0011] It is an object of the present invention to provide a processless heat-sensitive imaging material for making lithographic printing plates having excellent printing properties.  
 50 [0012] It is a further object of the invention to provide a heat sensitive imaging material for making lithographic printing plates with an improved lithographic latitude.  
 [0013] Further objects of the present invention will become clear from the description hereinafter.

### SUMMARY OF THE INVENTION

- 55 [0014] According to the present invention there is provided a heat-sensitive material for making lithographic printing plates comprising on a lithographic support an image-forming layer comprising a hydrophilic binder, a cross-linking agent for a hydrophilic binder and dispersed hydrophobic thermoplastic polymer particles, characterized in that said

image-forming layer is covered with a layer comprising at least one organic compound comprising cationic groups.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0015]** The organic compounds having cationic groups for use in connection with the present invention are preferably hydrophilic and may be low molecular weight compounds but are preferably polymers. Preferred compounds are those having one or more ammonium groups or amino groups that can be converted to ammonium groups in an acidic medium. An especially preferred type of cationic compounds are polysaccharides modified with one or more groups containing an ammonium or amino group.

**[0016]** Most preferred organic compounds having cationic groups are dextrans or pullulan wherein at least some of the hydroxy groups have been modified into one or more of the following groups:



wherein  $R^1$  represents an organic residue containing an amino or ammonium group, e.g. an amine substituted alkyl, an amine substituted alkylaryl etc..

**[0017]**  $R^2$  has one of the significances given for  $R^1$  or stands for  $-OR^3$  or  $-N(R^4)R^5$ , wherein  $R^3$  has one of the significances given for  $R^1$  and each of  $R^4$  and  $R^5$  which may be the same or different and have one of the significances given for  $R^1$ .

**[0018]** Pullulan is a polysaccharide that is produced by microorganisms of the *Aureobasidium pullulans* type (*Pullularia pullulans*) and that contains maltotriose repeating units connected by a  $\alpha$ -1,6 glycosidic bond. Pullulan is generally produced on industrial scale by fermentation of partially hydrolysed starch or by bacterial fermentation of sucrose. Pullulan is commercially available from e.g. Shodex, Pharmacosmos.

**[0019]** Examples of dextrans or pullulan suitable for use in accordance with the present invention are dextrans or pullulan wherein some of the hydroxyl groups have been modified in one of the groups shown in table 1.

Table 1

no.	modified group
1	$-O-CH_2-CH_2-NH_2$
2	$-O-CO-NH-CH_2-CH_2-NH_2$
3	$-O-CO-NH-CH_2-CH_2-N(CH_2-CH_2-NH_2)_2$
4	$-O-CH_2-CH_2-NH-CH_2-CH_2-NH_2$
5	$-O-CH_2-CH_2-NH-CH_2-CHOH-CH_2-N^+(CH_3)_3 Cl^-$
6	$-O-(CH_2-CH_2-O)_n-CH_2-CH_2-NH_2$ wherein n represents an integer from 1 to 50
7	$-O-CO-NH-CH_2-CH_2-NH-CH_2-CHOH-CH_2-N^+(CH_3)_3 Cl^-$
8	$-O-CH_2-CH_2-N(CH_2-CH_3)_2 \cdot HCl$
9	$-O-CH_2-CH_2-N(CH_2-CH_2-NH_2)_2$
10	$-O-CONH-CH_2-CH_2-N(CH_2-CH_2-NH_2)_2$
11	$-O-CONH-(CH_2-CH_2-O)_n-CH_2-CH_2-NH_2$

**[0020]** The modified dextrans or pullulan can be prepared by a reaction of a dextran with e.g. alkylating agents, chloroformates, acid halides, carboxylic acids etc..

**[0021]** The organic compound having one or more cationic groups according to the invention is preferably provided in an amount of 10 to 5000 mg/m<sup>2</sup> and more preferably in an amount of 20 to 1000 mg/m<sup>2</sup>.

**[0022]** According to the present invention to improve sensitivity and throughput and to avoid scumming an imaging element is provided comprising preferably hydrophobic thermoplastic polymer particles with an average particle size between 40nm and 2000nm. More preferably the hydrophobic thermoplastic polymer particles are used with an average particle size of 40nm to 200nm. Furthermore the hydrophobic thermoplastic polymer particles used in connection

with the present invention preferably have a coagulation temperature above 50°C and more preferably above 70°C. Coagulation may result from softening or melting of the thermoplastic polymer particles under the influence of heat. There is no specific upper limit to the coagulation temperature of the thermoplastic hydrophobic polymer particles, however the temperature should be sufficiently below the decomposition temperature of the polymer particles. Preferably the coagulation temperature is at least 10°C below the temperature at which the decomposition of the polymer particles occurs. When said polymer particles are subjected to a temperature above the coagulation temperature they coagulate to form a hydrophobic agglomerate in the hydrophilic layer so that at these parts the hydrophilic layer becomes hydrophobic and oleophilic.

**[0023]** Specific examples of hydrophobic polymer particles for use in connection with the present invention have a T<sub>g</sub> above 80°C. Preferably the polymer particles are selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, polyesters, polyurethanes, polyacrylonitrile, polyvinyl carbazole etc., copolymers or mixtures thereof. Most preferably used are polystyrene, polymethylmethacrylate or copolymers thereof.

**[0024]** The weight average molecular weight of the polymers may range from 5,000 to 5,000,000g/mol.

**[0025]** The polymer particles are present as a dispersion in the aqueous coating liquid of the image-forming layer and may be prepared by the methods disclosed in **US-P- 3 476 937**. Another method especially suitable for preparing an aqueous dispersion of the thermoplastic polymer particles comprises:

- dissolving the hydrophobic thermoplastic polymer in an organic water immiscible solvent,
- dispersing the thus obtained solution in water or in an aqueous medium and
- removing the organic solvent by evaporation.

**[0026]** The amount of hydrophobic thermoplastic polymer particles contained in the image-forming layer is preferably between 2 and 40 % by weight and more preferably between 10 and 20 % by weight of the total weight of said layer.

**[0027]** Suitable hydrophilic binders for use in an image-forming layer in connection with this invention are water soluble (co)polymers for example synthetic homo- or copolymers such as polyvinylalcohol, a poly(meth)acrylic acid, a poly(meth)acrylamide, a polyhydroxyethyl(meth)acrylate, a polyvinylmethylether or natural binders such as gelatin, a polysaccharide such as e.g. dextran, pullulan, cellulose, arabic gum, alginic acid, inuline or chemically modified inuline.

**[0028]** A cross-linked hydrophilic binder in the heat-sensitive layer used in accordance with the present embodiment also contains substances that increase the mechanical strength and the porosity of the layer e.g. oxide particles having an average diameter of at least 100 nm. Incorporation of these particles gives the surface of the cross-linked hydrophilic layer a uniform rough texture consisting of microscopic hills and valleys. Preferably these particles are oxides or hydroxydes of beryllium, magnesium, aluminium, silicon, gadolinium, germanium, arsenic, indium, tin, antimony, tellurium, lead, bismuth or a transition metal. Particularly preferable is titanium dioxide, used in 20 to 95 % by weight of the heat-sensitive layer, more preferably in 40 to 90% by weight of the heat-sensitive layer.

**[0029]** The image-forming layer also comprises crosslinking agents. such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetraalkylorthosilicate. The latter is particularly preferred.

**[0030]** The imaging element can further include a compound capable of converting light to heat. Suitable compounds capable of converting light into heat are preferably infrared absorbing components having an absorption in the wavelength range of the light source used for image-wise exposure. Particularly useful compounds are for example dyes and in particular infrared dyes as disclosed in **EP-A- 908 307** and pigments and in particular infrared pigments such as carbon black, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides and oxides structurally related to the bronze family but lacking the A component e.g. WO<sub>2.9</sub>. It is also possible to use conductive polymer dispersion such as polypyrrole or polyaniline-based conductive polymer dispersions. The lithographic performance and in particular the print endurance obtained depends i.a.on the heat-sensitivity of the imaging element. In this respect it has been found that carbon black yields very good and favorable results.

**[0031]** A light-to-heat converting compound in connection with the present invention is most preferably added to the image-forming layer but at least part of the light-to-heat converting compound may also be comprised in a neighbouring layer.

**[0032]** The imaging layer preferably contains surfactants which can be anionic, cationic, non-ionic or amphoteric. Perfluoro surfactants are preferred. Particularly preferred are non-ionic perfluoro surfactants. Said surfactants can be used alone or preferably in combination.

**[0033]** The weight of the imaging layer ranges preferably from 0.5 to 20 g/m<sup>2</sup>, more preferably from 3 to 15 g/m<sup>2</sup>.

**[0034]** The lithographic base according to the present invention can be aluminum e.g. electrochemically and/or mechanically grained and anodised aluminum.

**[0035]** Furthermore in connection with the present invention, the lithographic base can be a flexible support. As flexible support in connection with the present embodiment it is particularly preferred to use a plastic film e.g. substrated polyethylene terephthalate film, polyethylene naphthalate film, cellulose acetate film, polystyrene film, polycarbonate film, polyethylene film, polypropylene film, polyvinyl chloride film, polyether sulphone film. The plastic film support may

be opaque or transparent. The plastic film is preferably subbed with subbing layers as described in **EP-A- 619 524**, **EP-A- 619 525** and **EP-A- 620 502**.

**[0036]** Still further paper or glass of a thickness of not more than 1.2 mm can also be used.

**[0037]** In accordance with the present invention the imaging element is image-wise exposed. During said exposure, the exposed areas are converted to hydrophobic and oleophilic areas while the unexposed areas remain hydrophilic.

**[0038]** Said image-forming can be realized by direct thermal recording wherein the thermal transfer is effected by heat radiation, heat conductivity or inductive heat transport. It is believed that on the heated areas the hydrophobic polymer particles coagulate and form a hydrophobic area while on the non-heated areas the hydrophobic polymer particles remain unchanged and said area remains hydrophilic.

**[0039]** Said image-forming can also be effected by irradiation with high intensity light. The heat-sensitive material should then comprise a compound capable of converting light into heat.

**[0040]** Image-wise exposure in connection with the present invention is preferably an image-wise scanning exposure involving the use of a laser or L.E.D. Preferably used are lasers that operate in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared.

**[0041]** According to the present invention the plate is then ready for printing without an additional development and can be mounted on the printing press.

**[0042]** According to a further method, the imaging element is first mounted on the printing cylinder of the printing press and then image-wise exposed directly on the press. Subsequent to exposure, the imaging element is ready for printing.

**[0043]** The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. In this option the printing plate is soldered in a cylindrical form by means of a laser. This cylindrical printing plate which has as diameter the diameter of the print cylinder is slid on the print cylinder instead of mounting a conventional printing plate. More details on sleeves are given in "Grafisch Nieuws", 15, 1995, page 4 to 6.

**[0044]** The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

#### EXAMPLES

**[0045]** On top of an aluminum substrate was coated the IR-sensitive layer to a wet coating thickness of 70  $\mu\text{m}$  from a solution having the following composition:

17.28 g of a  $\text{TiO}_2$  dispersion in water (average particle size 0.3 to 0.5  $\mu\text{m}$ )-25.97 % w/w.

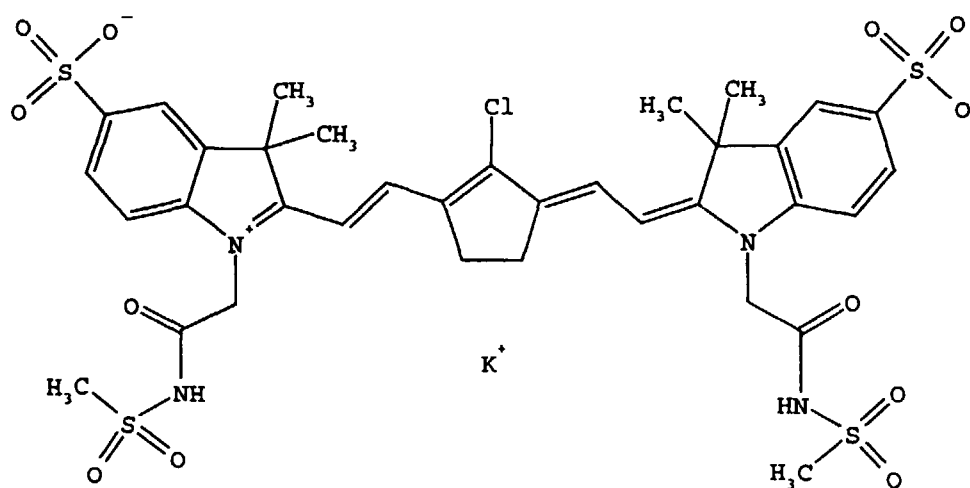
8.44 g of hydrolyzed tetramethylorthosilicate in water -24.86% w/w.

1 g of wetting agent-5 % w/w.

9.11 g of non-ionic stabilized polystyrene latex-12.8 % w/w.

0.20 g of IR-dye A

33.95 of water.



IR-Dye A

**[0046]** This layer was hardened for 12 hours at 67 °C and 50 % R.H. Imaging element I was so obtained. Imaging elements II, III, IV, V, VI were obtained by coating on top of the imaging element I a hydrophilic layer from a 1 %w/w solution from a diethylaminoethoxylated dextran (Dormacid <sup>TM</sup> from Pfeifer and Langen). The hydrophilic layer was coated to a dry coating thickness of 0.05 , 0.10, 0.25, 0.50, 0.75 g/m<sup>2</sup> respectively.

**[0047]** Imaging element VII was prepared by treating imaging element I with a 1 %w/w solution in water of Dormacid <sup>TM</sup> by rinsing with a cotton pad soaked in the described solution.

**[0048]** The resulting imaging elements were imaged on a CREO 3244 Trendsetter <sup>TM</sup> at 2400 dpi operating at a drum speed of 140 rpm and a laser output of 15.5 Watt.

**[0049]** After imaging, the plates were mounted on a GTO 52 press using K + E 800 as ink and rotamatic as fountain.

**[0050]** Subsequently the press was started by allowing the print cylinder with the imaging element mounted thereon to rotate. The dampener rollers of the press were first dropped on the imaging element so as to supply dampening liquid to the imaging element and after 10 revolutions of the print cylinder , the ink rollers were dropped to supply ink. After 10 further revolutions ink was feeded. The Dmin and the dot areas of the 50 % screen at 200 lpi were measured at prints 5, 25, 50. The Dmin and the dot area were measured with a Macbeth RD918-SB<sup>TM</sup>.

Table 1

Dmin			
Element	print 5	print 25	print 50
I	0.19	0.11	0.06
II	0.00	0.00	0.01
III	0.00	0.00	0.01
IV	0.00	0.00	0.01
V	0.01	0.01	0.01
VI	0.00	0.01	0.01
VII	0.00	0.00	0.00

Table 2

Dot area			
Element	print 5	print 25	print 50
I	92	96	97
II	70	73	75
III	70	74	75
IV	66	62	74
V	69	74	74
VI	71	74	75
VII	72	74	75

**[0051]** From these results, it is clear that an additional hydrophilic top layer of a diethylaminoethoxylated dextran improves the lithographic characteristics, i.e. less toning at start-up and lower dot gain.

## Claims

1. A heat-sensitive material for making lithographic printing plates comprising on a lithographic support an image-forming layer comprising a hydrophilic binder, a cross-linking agent for a hydrophilic binder and dispersed hydro-

phobic thermoplastic polymer particles, characterized in that said image-forming layer is covered with a layer comprising at least one organic compound comprising cationic groups.

2. A heat-sensitive material according to claim 1 wherein said organic compound is a hydrophylic polymer having one or more ammonium groups or a low molecular weight hydrophylic organic compound having one or more ammonium groups.
3. A heat-sensitive material according to claim 2 wherein said hydrophilic polymer is a modified polysaccharide having groups containing an amino or ammonium group.
4. A heat-sensitive material according to claim 3 wherein said modified polysaccharide is a dextran or a pullulan containing an amino or ammonium group.
5. A heat-sensitive material according to any of claims 1 to 4 wherein said organic compound is comprised in said imaging element in an amount between 0.02 and 1.00 g/m<sup>2</sup>.
6. A heat-sensitive material according to any of claims 1 to 5 wherein said heat-sensitive material comprises a compound capable of converting light into heat.
7. A heat-sensitive material according to claim 6 wherein said compound capable of converting light into heat is an IR sensitive dye or pigment.
8. A heat-sensitive material according to any of claims 1 to 6 wherein said image forming layer is present in an amount ranging from 0.5 to 20 g/m<sup>2</sup>.
9. A heat-sensitive material according to any of claims 1 to 8 wherein said image forming layer comprises oxides or hydroxydes of beryllium, magnesium, aluminium, silicon, gadolinium, germanium, arsenic, indium, tin, antimony, tellurium, lead, bismuth, titanium or a transition metal.
10. A method for making a lithographic printing plate comprising the step of image-wise exposing to heat a heat-sensitive material according to any of claims 1 to 9 thereby resulting in an increase in hydrophobicity and oleophilicity of the exposed areas without loss of hydrophilicity of the non-imaged parts.
11. A method for making a lithographic printing plate according to claim 10 wherein an image is formed by direct thermal recording.
12. A method for making lithographic printing plates according to claim 10 or 11 wherein the heat-sensitive material is mounted on a printing press.
13. A method for making lithographic printing plates comprising the step of image-wise exposing to IR-radiation a heat sensitive material according to claim 7 thereby resulting in an increase in hydrophobicity and oleophilicity of the exposed areas without loss of hydrophilicity of the non-imaged parts.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 00 20 1854

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.7)
X	GB 2 325 055 A (AGFA GEVAERT NV) 11 November 1998 (1998-11-11)	1,2	B41C1/10 B41M5/36
Y	* page 19, line 4 - line 5 * ---	1-13	
X	EP 0 816 070 A (AGFA GEVAERT NV) 7 January 1998 (1998-01-07)	1-13	
Y	* column 3, line 37 * ---	1-13	
X	EP 0 849 090 A (AGFA GEVAERT NV) 24 June 1998 (1998-06-24) * page 5, line 7 * * page 6, line 47 - line 52 * ---	1-13	
Y	WO 94 16904 A (UYTTERHOEVEN HERMAN JOZEF ;AGFA GEVAERT NV (BE); BLOODWORTH ROBERT) 4 August 1994 (1994-08-04) * column 1 *	3,4	
Y	EP 0 703 499 A (MINNESOTA MINING & MFG) 27 March 1996 (1996-03-27) * page 6, line 47 - line 53 * ---	1-5	
A	EP 0 514 990 A (AGFA GEVAERT NV) 25 November 1992 (1992-11-25) * the whole document * -----	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B41C B41M G03F
Place of search	Date of completion of the search	Examiner	
THE HAGUE	26 June 2000	Bacon, A	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone		T : theory or principle underlying the invention	
Y : particularly relevant if combined with another document of the same category		E : earlier patent document, but published on, or after the filing date	
A : technological background		D : document cited in the application	
O : non-written disclosure		L : document cited for other reasons	
P : intermediate document		& : member of the same patent family, corresponding document	

EPO FORM 1503 03/82 (P/MC01)



**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 1854

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-06-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2325055 A	11-11-1998	WO 9851496 A EP 0981442 A	19-11-1998 01-03-2000
EP 0816070 A	07-01-1998	NONE	
EP 0849090 A	24-06-1998	JP 10193824 A	28-07-1998
WO 9416904 A	04-08-1994	NONE	
EP 0703499 A	27-03-1996	US 5506090 A CN 1141444 A JP 8114922 A US 5939237 A	09-04-1996 29-01-1997 07-05-1996 17-08-1999
EP 0514990 A	25-11-1992	DE 69200697 D DE 69200697 T JP 5212986 A US 5402725 A	05-01-1995 08-06-1995 24-08-1993 04-04-1995