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### (54) Radiation sensitive composition

(57) The invention discloses a radiation sensitive composition which comprises a novolac resin, a copolymer with metal ions, acid generators and radiation absorptive dyes. The composition is coated on an applicable substrate. The coated substrate is baked, exposed

and developed to produce an image, which has desirable hardness, abrasion-resistance, adhesiveness and print durability.

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#### Description

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Field of the Invention

5 **[0001]** This invention generally relates to radiation sensitive compositions used in lithographic printing plates.

Description of Prior Art

[0002] The feature of lithographic printing is that the image area retaining ink and non-image area retaining water are on a lithographic printing plate, wherein the image area retains oil and repels water and the non-image area retains water and repels oil. The operation of lithographic printing uses the immiscibility of oil (oily materials or ink) and water. A non-image of a lithographic printing plate is firstly moistened with water to form a water-retained and oil-repelled water film. Then ink is applied to the lithographic printing plate wherein the image area accepts ink. Pressure is applied during printing process such that the ink on the image area containing images or texts is transferred to the surface of papers or printable objects via a blanket. Typically, the ink is firstly transferred to the blanket, the intermediate material. Then the ink transferred onto the blanket is further transferred to the printable surface of a material such as papers, cloths, plastics or metals.

**[0003]** The preparation of pre-sensitized plate (PS plate) may start with electrolyzing or polishing a surface of an aluminum plate to form a plurality of grains required for printing. The light sensitive or heat sensitive radiation sensitive composition is coated on the grains of the aluminum plate to form a radiation sensitive coating. The radiation sensitive coating is baked and cured. Following that, a negative having pre-determined images and texts is transferred to the radiation sensitive coating via exposure and develop process to produce a printing plate for printing the images and texts on printable objects.

[0004] In recent years, digital technologies using computer for processing and outputting image data are widely utilized. Various applicable new image output methods are utilized in the market. There are lithographic printing technologies skipping process using a negative. Digital images in a computer are directly transferred to a radiation sensitive coating via expose and develop process to produce printing plate for printing images and texts on printable objects. Thus the operation of plate production is significantly simplified, which increases the printing efficiency and lowers production cost. Such technologies are called Computer to Plate (CTP). The methods for producing the printing plate applicable to CTP have new issues to resolve.

**[0005]** Upon a radiation sensitive composition coated on a surface of an aluminum plate used for lithographic printing is exposed, the exposed portion is alkali soluble and is removed during the develop process to form a positive plate. On the other hand, exposed portion is cured and becomes alkali non-soluble to form a negative plate. Under the above two circumstances, the image area accepts ink or is lipophilic and the non-image area accepts water or is hydrophilic. Weather a light-sensing plate is categorized as positive or negative type depends on the radiation sensitive composition coated on the aluminum plate.

**[0006]** The radiation sensitive composition mentioned above mainly composed of the following materials: radiation absorptive dyes (a light sensitive agent or a heat sensitizing agent), acid generators, novolac resins (film-forming resins), copolymers, solvents, and other assistants.

**[0007]** The prior art disclosed in the U.S. Pat. No. 6,063,544 is a positive plate coated with mixtures of novolac resin or cresol-formaldehyde or polyhydroxystyrene and infrared light absorptive dyes. In addition, the U.S. Pat. No. 5,372,907, 5,372,915, 5,340,699, 5,491,046 disclose plates coated with mixtures of novolac resin, cresol novolac resin, infrared light absorptive dyes or colorant and latent Bronsted acid. When the plates are exposed to infrared light radiation, the latent Bronsted acid is decomposed to generate a material catalyzing crosslinking reactions of different novolac resins (such as a novolac resin and a cresol resin) in order to cure the mixtures in the exposed areas. Further, the exposed printing plate is heated to enhance curing of the exposed .coating and becomes insoluble to alkaline developer solution, where the non-exposed area remains soluble to developer solution. The U.S. Pat. No. 5,919,601 1 discloses a radiation sensitive composition composed of binder resins, crosslinking agents, thermal-activated acid generators and infrared light absorbents. The composition is exposed to infrared light. Then the acid generators are decomposed to release acid ions to catalyze crosslinking reactions of binder resins via crosslinking agents.

**[0008]** The disadvantage of the above technologies in common is that the developed image area of the printing plate lacks of integrity and is not durable for printing for a long time which leads to undesirable image resolution and printing qualities.

**[0009]** In order to improve commercial competiveness, printing operators are required to increase plate making efficiency and printing qualities, there is a demand for faster sensitivity of the radiation sensitive coating on a printing plate. In other words, the required exposure energy is desired to be lower and the required exposure time is desired to be shorter. In addition, the exposed portion is desired to be easier removed by a developer solution during develop process. Non-exposed portion is desired to have higher resistance to soak in and washed by a developer solution. That means

the non-exposed portion is desired to have higher tolerance on temperature, concentration of the developer solution as well as soaking and washing time during develop process. Whilst, it is also desired to maintain fine resolution, ink absorption and abrasion-resistance of the radiation sensitive coating. Further, it is desired to increase adhesiveness between the radiation sensitive coating and aluminum plate.

#### SUMMARY OF THE INVENTION

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**[0010]** The objective of the invention is to provide a radiation sensitive composition for producing images. The radiation sensitive composition may effectively improve hardness, abrasion-resistance, adhesiveness and print durability without interfering exposure sensitivity and developing latitude.

**[0011]** To achieve the above objective, the inventor conducted researches in order to provide a copolymer having metal ion structural unit represented by formula (I) in the following. The copolymer is added as part of the formula of a radiation sensitive composition to offer high sensitivity and developing latitude and effectively increases hardness, abrasion-resistance, adhesiveness and print durability of the radiation sensitive coating.

# formula (I)

 $M \rightarrow \frac{1}{n}$ 

wherein M is a zinc , magnesium, or copper divalent metal ion, X is O, S, N, or polyalkylene oxide group , and n≥1. **[0012]** The radiation sensitive composition of the present invention comprises copolymers polymerized with specific monomers for enhancing hardness and adhesiveness, which significantly increases hardness, abrasion-resistance and adhesiveness of radiation sensitive coating while maintaining exposure sensitivity and developing latitude. Thus, print durability of lithographic printing is considerably enhanced.

#### DETAILED DESCRIPTION OF THE INVENTION

[0013] The present invention provides a radiation sensitive composition used for forming an image layer. The composition is used as a coating on a positive and negative plate. The composition is composed of a mixture comprising (a) 30~95 weight percent of a novolac resin (film forming resin), (b) 4~70 weight percent of a copolymer, (c) 0.1~45 weight percent of a radiation absorptive dye, and (d) 0.1~15 weight percent of an acid generator. The composition of the invention further comprises solvents and additive agents.

**[0014]** The present invention also provides a method for producing an image. The method comprises: (I) coating an imaging layer on a substrate, wherein the imaging layer is composed of (a) a novolac resin, (b) a copolymer, (c) a radiation absorptive dye, (d) an acid generator, wherein the imaging layer further comprises a solvent and an additive agent; (II) drying the imaging layer; (III) exposing an image forming area of the imaging layer under an energy source emitting sufficient light beams, wherein the light beams can be UV/Vis light beams with a wave length of 320nm~750nm or IR light beams with a wave length of 750nm~1350nm; and (IV) soaking the image forming area in a developer solution for removing the exposed portion from the substrate.

**[0015]** The novolac resins applicable to the present invention include phenol, o-cresol, m-cresol, p-cresol, 2-naphthol, phenol derivatives or a mixtures composed of at least two above mentioned compounds, and aldehyde condensation products such as formaldehyde, acetaldehyde, other aliphatic or aromatic aldehyde etc. The product, the novolac resin, preferably has a weight average molecular weight in a range between 300 ~ 400,000.

**[0016]** The copolymers applicable to the present invention are composed of a (meth)acrylic acid monomer such as methyl methacrylate (MMA), methacrylic acid (MAA), lauryl (meth)acrylate, isobutyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, ethylhexyl (meth)acrylate, dodecyl 2-(meth) acrylate etc., styrene and the derivatives such as  $\alpha$ -methylstyrene, 4-hydroxystyrene, 4-hydroxymethylstyrene, Methylstyrene with halogen, maleic anhydride, acrylonitrile and N-substituted maleimide monomer, wherein N-substituted maleimide monomer is N-phenylmaleimide, 4-hydroxy-phenylmaleimide, N-(2,3-dimethylphenyl) maleimide. The above monomers are polymerized based on different composition combination and ratios used as a light sensing coating. The copolymers of the present invention have metal structural units, wherein structure of a reactive monomer having metal ions is represented as formula (II):

## formula ( II )

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 $R_1$ 

wherein  $R_1$  and  $R_2$  are H or  $CH_3$ , M is a zinc , magnesium, copper divalent metal ion, X and Y are O, S, or N polyalkylene oxide group. Among which, a di(meth)acrylate monomer and the derivatives of a diacrylate monomer having metal ions is zinc diacrylate (ZDA), zinc dimethacrylate (ZDMA), magenesium diacrylate, copper diacrylate, zinc thiodiacrylate and zinc thiodimethylacrylate, etc.

**[0017]** The radiation absorptive dyes applicable to the present invention largely include light sensitive dyes and heat sensitive dyes. The light sensitive dyes mainly include 1,2-naphthoquinonediazide-4-sulfonyl chloride or 1,2- naphthoquinonediazide-5-sulfonyl chloride and esterification condensates of polyhydroxy compounds. The heat sensitive dyes mainly include dyes with wave length of 700-900nm, such as cyanine dyes, polymethine dyes, naphthoquinone dyes, phthalocyanine dyes, anthraquinone dyes, or indoaniline metal complex dyes, etc.

[0018] Acid generators applicable to the present invention generate protic acids after exposing to heat or light generated by light within an infrared light spectrum. The generated protic acid is used in photo decomposition of light sensing materials of the copolymers in the exposed area. Compounds generating protic acids via thermo chemistry are disclosed in U.S. Pat. No. 5,466,557. The US patent is incorporated in the present application as references. Applicable compounds include haloalkyl compounds such as haloalkyl-substituted s-triazinehaloalkyl, haloalkyl 2-pyrone, haloalkyl oxazole, haloalkyl oxadiazole andhaloalkyl thiazole, etc. These compounds generally have functional group such as trihalomethyl, which may produce polyhalomethyl-substituted hydrohalic acid when receiving the heat of infrared radiation. The most applicable acid generators may be selected from a variety of (trichloromethyl) -triazine, that is, it is preferred to select from, but not to limit to 2,4,6-(trichloromethyl)-1,3,5-triazine, 2,4-(trichloromethyl)-6-(3,5-methoxyphenyl)-1,3,5-triazine, 2,4-(trichloromethyl)-6-(3,5-methoxyphenyl)-1,3,5-triazine, 2,4-(trichloromethyl)-6-(methoxynaphenyl)-1,3,5-triazine, 2,4-(trichloromethyl)-6-(methoxynaphenyl)-1,3,5-triazine, 2,4-(trichloromethyl)-6-(methoxynaphenyl)-1,3,5-triazine, 2,4-(trichloromethyl)-6-(4-methoxystyryl)-1,3,5-triazine, etc.

**[0019]** The compounds generally have trihalomethyls and generate polyhalomethyls with halogen acids upon a compound is under heat from IR radiation. The most frequently used acid products are selected from various trichloromethyltriazines, preferably selected from but not limited to tris-trichlorotriazine, bis(trimethylphenyl)triazine, bis(trichloro)-omethoxyphenyltriazine or bis(trichloro)-p-methoxyphenyltriazine,bis(trichloro)(3,5-dimethoxylphenyl)triazine, is(trichloro)naphthyltriazine,bis(trichloro)(5-methoxynaphthyl)triazine, bis(trichloro)styryl)triazine and bis(trichloro)(4-methoxylstyryl)triazine, etc.

**[0020]** The solvent used by the present invention is selected from ethanols, esters, ketones, ethers, carboxamides, aromatics and mixtures thereof and in particular 1-methoxyl-2- ethanol, 1-methoxyl-2- propanol, ethyl glycol acetate, ethyl acetate, acetone, butanone, diisobutyl ketone, methyl isobutyl ketone, cyclohexanone, toluene, xylene, 1-propanol, isopropanol, tetrahydrofuran, butyrolactone, methyl lactate, dimethyl amide and mixtures thereof.

**[0021]** The additive agents used by the present invention include additives such as surfactants, coloring agents and wetting agents. The coloring agent is used for differentiating image on the printing plate after the develop process. The coloring agent applicable to the present invention include oil-soluble dyes or basic dyes such as crystal violet, malachite green, victoria blue, methylene blue, ethyl violet, oil blue 603/613, or rhodamine B etc. and mixtures thereof.

**[0022]** The present invention is detailed by the following examples:

<Example 1> The copolymer synthesis

[0023] The synthesis method of the copolymer and the monomer ratio are listed but not limited to the following.

	monomer composition (wt%)						
copolymer No.	PMI MMA St AN ZI						
P-1	35	30	0	35	0		
P-2	35	25	0	35	5		
P-3	35	20	0	35	10		
P-4	35	0	30	35	0		
P-5	35	0	25	35	5		
P-6	35	0	20	35	10		

[0024] Note: PMI=N-phenyl maleimide; MMA= methyl methacrylate; St= styrene; AN= acrylonitrile; ZDA=zinc diacrylate

(The synthesis method of the copolymer)

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[0025] 35g PMI, 30g MMA, 35g AN, 1g initiator (Azobisisobutyronitrile, AIBN) and 200g solvent (Dimethyl Formamide, DMF) are placed in a 500ml four-necked flask. The four-necked flask equipped with a stirring blade, a thermometer, a reflux condenser and a nitrogen inlet. The reaction temperature is controlled at 70°C for 24 hours. After cooling to room temperature, the resulting reaction mixture was poured into 6kg of water to precipitate the copolymer in the form of powder. The copolymer is filtered and dried to give the copolymer (copolymer P-1). Copolymers with other different compositions can also be obtained by the above method.

<Example 2> Preparation of the radiation sensitive composition and a heat sensitive CTP printing plate

[0026] The heat sensitive radiation sensitive composition of the present example is generated by stirring the following components until the components are totally dissolved in the solvents. The components include 20g novolac resin -Rezicure5200 (high purity degree of a m-cresol novolac resin from SpecialCheme Company), 6g novolac resin -DUR-ITE® SD-1508 (a novolac resin composed mainly of bisphenol from Hexion Company), 9.0g copolymer (copolymer P-1), 0.8g radiation absorptive dyes -cyanine dyes IR dye 23b[PCAS] (dyes reacted under IR light from PCAS Company), 0.24g 2,4-(trichloromethyl)-6-(4-methoxystyryl)-1,3,5-triazine, 0.5g coloring agent -victoria blue, 0.5g coloring agent -crystal violet lactone, 6ml solvent ethyl acetate, and 104g solvent ethyl glycol acetate.

[0027] Provide an aluminum plate with hydrophilic treatment. The above mentioned heat sensitive radiation sensitive composition is coated on the aluminum plate with coating thickness of 1.8 g/m². The coated aluminum plate is baked under 100°C for 4 minutes and cured under 50°C for 24 hours to generate a positive heat sensitive CTP printing plate. [0028] Following exposure, several developer solutions are used for develop process and the comparison result is listed in the following table. The exposure process and develop process use the positive heat sensitive CTP printing plate generated in the Example 2, a Screen PTR-8600 900rpm exposure machine (from Screen Company). The range of exposure percentage is 50%~90% and the exposure step condition is 5%. Among which, the developer solutions Kodak Premium, Kodak Plus are from Kodak Company, and Agfa Energy is from Agfa Company.

developer solution	Kodak Premium	Kodak Plus	Agfa Energy
develop temperature (°C)	23.0	23.0	24.0
develop time (seconds)	30	35	20
clarity (%)	60	65	60
all pass range (%)	60~90	70~90	60~90

**[0029]** <Example 3> The preparation of a radiation sensitive composition and a heat sensitive CTP printing plate printing plate in the present example is largely identical with the preparation of the positive heat sensitive CTP printing plate in the example 2, wherein the difference is that the copolymer used is the sample P-2. The procedure of Example 2 was repeated except that copolymer P-1 was replaced with copolymer P-2.

<Examples 4> The preparation of a radiation sensitive composition and a heat sensitive CTP printing plate

**[0030]** The preparation of the printing plate in the present example is largely identical with the preparation of the positive heat sensitive CTP printing plate in the example 2, wherein the difference is that the copolymer used is the sample P-3. The procedure of Example 2 was repeated except that copolymer P-1 was replaced with copolymer P-3.

<Example 5> The preparation of a radiation sensitive composition and a heat sensitive CTP printing plate

**[0031]** The preparation of the printing plate in the present example is largely identical with the preparation of the positive heat sensitive CTP printing plate in the example 2, wherein the difference is that the copolymer used is the sample P-4. The procedure of Example 2 was repeated except that copolymer P-1 was replaced with copolymer P-4.

<Example 6> The preparation of a radiation sensitive composition and a heat sensitive CTP printing plate

**[0032]** The preparation of the printing plate in the present example is largely identical with the preparation of the positive heat sensitive CTP printing plate in the example 2, wherein the difference is that the copolymer used is the sample P-5. The procedure of Example 2 was repeated except that copolymer P-1 was replaced with copolymer P-5.

<Example 7> The preparation of a radiation sensitive composition and a heat sensitive CTP printing plate

**[0033]** The preparation of the printing plate in the present example is largely identical with the preparation of the positive heat sensitive CTP printing plate in the example 2, wherein the difference is that the copolymer used is the sample P-6. The procedure of Example 2 was repeated except that copolymer P-1 was replaced with copolymer P-6.

<Example 8> The preparation of a radiation sensitive composition and a heat sensitive CTP printing plate

**[0034]** The preparation of the printing plate in the present example is largely identical with the preparation of the positive heat sensitive CTP printing plate in the example 2, wherein the difference is that no copolymer is used for serving as a blank example for comparing effects adding copolymers. The present example uses 24.5g novolac resin -Rezicure5200, 10.5g novolac resin -DURITE® SD-1508, 0.8g radiation absorptive dyes -cyanine dyes IR dye 23b [PCAS], 0.24g 2,4-(trichloromethyl)-6-(4-methoxystyryl)-1,3,5-triazine, 0.5g coloring agent victoria blue, 0.5g coloring agent -crystal violet lactone, 6ml solvent ethyl acetate, and 104g solvent ethyl glycol acetate.

**[0035]** The positive heat sensitive CTP printing plates generated in Example 2 to Example 8 are put through exposure and develop tests. The develop test uses developer solution Kodak premium, at temperature of 23°C and develop time is 30 seconds. The 50% dot formation test uses iCPlate2 [X-rite] printing plate measuring apparatus (from X-Rite Company). The result is categorized and listed in the following.

No/Energy (mJ/cm <sup>2</sup> )	146	155	165	176	188	203	220
Example 2	52.5	52.0	51.3	50.4	49.5	49.1	48.0
Example 3	52.3	51.7	51.1	50.2	49.4	48.5	47.8
Example 4	51.8	51.6	50.8	50.0	49.7	48.6	47.5
Example 5	52.6	51.7	51.4	50.4	49.4	48.8	48.2
Example 6	52.4	51.5	51.1	49.9	49.2	48.3	47.9
Example 7	52.1	51.2	49.8	49.5	49.1	48.0	47.5
Example 8	53.0	52.5	51.4	50.8	50.1	49.8	48.5

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[0036] The X-rite 528 color meter (from X-rite Company) measures thinning difference of samples from Example 2 to Example 8 (which means the difference of light sensing layer before and after the test). The reference point for measuring clean point is concluded by adding alcohol drops onto the plate until there is no color change and then the corresponding clean point is measured. Typically the light sensing layer has colorants, such as blue colorant. When the light sensing layer has residues on the plate, the alcohol dissolves the colorant within the light sensing layer. In other words, alcohol is used for testing if there are residues of the light sensing layer on the plate. In addition, finger touch is the main reason causing printing surface falling off or scratching. A surface hardness test is applied to the product graded by standard pencil hardness to differentiate product surface hardness. The test uses 3M#610 tape sticking to printing patterns. The

tape is pressed firmly to assure no air is left between the sticking surface between the tape and the printing patterns. One minute after the tape sticking to the printing patterns, the tape is peeled from the printing patterns. If the printing patterns are not damaged, the adhesiveness is OK. If the printing patterns are torn by the tape, the adhesiveness is NG. The abrasion-resistance test uses abrasion tester and wet test method wherein the surface is rubbed repeatedly for 100 times and observed if any damage occurred to the surface. The result is graded by three categories undesirable, normal and desirable. Lastly, accelerated abrasion printing conditions are applied to test the maximum printing amount with commercially acceptable quality.

10	No.	Thinning Difference Percentage (%)	Clean point	Hardness (H)	adhesiveness	abrasion- resistance	print durability
	Example 2	0.11	146mJ/ cm <sup>2</sup>	4H	NG	undesirable	45000
15	Example 3	0.13	146mJ/ cm <sup>2</sup>	≥4H	ОК	desirable	100000
	Example 4	0.12	146mJ/ cm <sup>2</sup>	≥4H	ОК	desirable	120000
20	Example 5	0.12	146mJ/ cm <sup>2</sup>	4H	NG	normal	50000
	Example 6	0.12	146mJ/ cm <sup>2</sup>	≥4H	ОК	desirable	110000
	Example 7	0.13	146mJ/ cm <sup>2</sup>	≥4H	ОК	desirable	130000
	Example 8	0.27	146mJ/ cm <sup>2</sup>	3H	NG	undesirable	30000

[0037] According to the above data, it is concluded that the positive heat sensitive CTP printing plates of the present invention have high sensitivity and high alkali resistance. The added copolymers synthesized with zinc diacrylate (ZDA) do not have impact on the sensitivity and alkali resistance. of printing plate, where hardness, adhesiveness, abrasion-resistance and print durability are significantly improved. Without the copolymers added, the hardness, print durability and adhesiveness are undesirable.

#### **Claims**

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1. A radiation sensitive composition for applying on a substrate to form an image layer **characterized in that** the composition comprising copolymers having metal ion structural unit represented by the following formula (I):

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$$\left( \begin{array}{c} \\ \\ \\ \\ \end{array} \right) \times M \rightarrow n$$

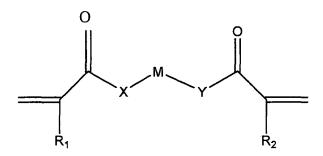
wherein M is a zinc , magnesiwn, or copper divalent metal ion, X is O, S, N, or polyalkylene oxide group , and n≥1.

2. The radiation sensitive composition of claim 1, wherein the reactive monomer of the copolymers having metal ion structural unit represented by the following formula (II):

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# formula (II)



- wherein  $R_1$  and  $R_2$  are H or  $CH_3$ , M is a zinc , magnesium, copper divalent metal ion, and X and Y are O, S, N, or polyalkylene oxide group.
  - **3.** The radiation sensitive composition of claim 1, which further comprises radiation absorptive dyes, solvents, surfactants, coloring agents, wetting agents, acid generators or mixtures thereof.
  - 4. The radiation sensitive composition of claim 1, wherein the substrate is a printing plate.



# **EUROPEAN SEARCH REPORT**

**Application Number** EP 10 01 3376

		ERED TO BE RELEVANT			
Category	Citation of document with ir of relevant pass	ndication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)	
Х	and fluorescence qu polythiophene/ZnO r through atom-transf polymerization and	hydrolysis", ENCE ELSEVIER SCIENCE 010-02-15), pages 177,	1	INV. B41C1/10 G03F7/038	
X	OF ZINC POLYMETHACE METHACRYLATE/METHYL COPOLYMER.",	METHACRYLATE AND STABILITY 1984, pages 239-250,	1	TECHNICAL FIELDS SEARCHED (IPC) B41C G03F	
A	EP 0 324 485 A2 (TO 19 July 1989 (1989- * page 2, line 52 - * page 4, line 51 - claims 1-5 *	07-19) page 3, line 12 *	1-4	4031	
	The present search report has	peen drawn up for all claims			
	Place of search	Date of completion of the search	<u> </u>	Examiner	
	Munich	8 December 2010	0e	chsner de Coninck	
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# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 10 01 3376

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.

08-12-2010

	Patent document cited in search report		Publication date		Patent family member(s)	Publication date
	EP 0324485	A2	19-07-1989	AU JP US	2842389 A 1182845 A 4999279 A	13-07-1989 20-07-1989 12-03-1991
9459						
O FORM P0459						

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#### REFERENCES CITED IN THE DESCRIPTION

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# Patent documents cited in the description

- US 6063544 A [0007]
- US 5372907 A [0007]
- US 5372915 A [0007]
- US 5340699 A [0007]

- US 5491046 A [0007]
- US 59196011 B [0007]
- US 5466557 A [0018]