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(54) Title: METHOD OF MAKING LITHOGRAPHIC PRINTING PLATES

(57) Abstract

A method for preparing a lithographic printing plate which involves providing a plate precursor comprising a grained and anodised aluminium substrate coated with a metallic layer, preferably a silver layer, deposited by means of an electroless deposition process, and imagewise exposing the precursor by means of a high intensity laser beam. On exposure of the plate precursor, removal of the metallic layer occurs in the exposed areas. The method provides press ready plates showing high image quality, good press properties and high durability on press, whilst eliminating the requirement for the use of intermediate film and developer chemistry.

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Method of making lithographic printing plates

This invention relates to the formation of images directly from electronically composed digital sources and is particularly concerned with the formation of images on lithographic printing plate precursors. More particularly, the invention relates to lithographic printing plate precursors which incorporate an imaging layer comprising metallic silver, and a method of preparing lithographic printing plates which does not require the use of chemical treatments.

Lithographic printing is a process of printing from surfaces which have been prepared in such a way that certain areas are capable of accepting ink (oleophilic areas), whereas other areas will not accept ink (oleophobic areas). The oleophilic areas form the printing areas while the oleophobic areas form the background areas.

Plates for use in lithographic printing processes may be prepared using a photographic material that is made imagewise receptive or repellent to ink upon photo-exposure of the photographic material and subsequent chemical treatment. However, this method of preparation, which is based on photographic processing techniques, involves several steps, and therefore requires a considerable amount of time, effort and expense.

Consequently it has, for many years, been a long term aim in the printing industry to form images directly from an electronically composed digital database, ie by a so-called "computer-to-plate" system. The advantages of such a system over the traditional methods of making printing plates are:

(i) the elimination of costly intermediate silver film and processing chemicals;
(ii) a saving of time; and
(iii) the ability to automate the system with consequent reduction in labour costs.

The introduction of laser technology provided the first opportunity to form an image directly on a printing plate precursor by scanning a laser beam across the surface of the precursor and modulating the beam so as to effectively turn it on and off. In this way, radiation sensitive plates comprising a high sensitivity polymer coating have been exposed to laser beams produced by water cooled UV argon-ion lasers and electrophotographic plates having sensitivities stretching into the visible spectral region have been successfully exposed using low powered air-cooled argon-ion, helium-neon and semiconductor laser devices.

Imaging systems are also available which involve a sandwich structure which, on exposure to a heat generating infra-red laser beam, undergoes selective (imagewise) delamination and subsequent transfer of materials. Such so-called peel-apart systems are generally used as replacements for silver halide films.

A digital imaging technique has been described in US Patent No 4911075 whereby a so-called driographic plate which does not require dampening with an aqueous fountain solution to wet the non-image areas during printing is produced by means of a spark discharge. In this case, a plate precursor comprising an ink-repellent coating containing electrically conductive particles coated on a conductive substrate is used and the coating is ablatively removed from the substrate. Unfortunately, however, the ablative spark discharge provides images having relatively poor resolution.

It is known to improve this feature by the use of lasers to obtain high resolution ablation as described, for example, by P E Dyer in "Laser Ablation of Polymers" (Chapter 14 of "Photochemical Processing of Electronic Materials", Academic Press, 1992, p359-385). Until recently, imaging via this method generally involved the use of high power carbon dioxide or excimer lasers. Unfortunately, such lasers are not well-suited to printing applications because of their high power consumption and excessive cost, and the requirement for high pressure gas handling systems. Recent developments have, however, led to the availability of more suitable infra-red diode lasers, which are compact, highly efficient and very economical solid state devices.

High power versions of such lasers, which are capable of delivering up to 3000 mJ/cm^2, are now commercially available.

Coatings which may be imaged by means of ablation with infra-red radiation have previously been proposed. Thus, for example, a proofing film in which an image is formed by imagewise ablation of a coloured layer on to a receiver sheet is described in PCT Application No 90/12342. This system is, however, disadvantageous in requiring a physical transfer of material in the imaging step, and such methods tend to give rise to inferior image resolution.

Much superior resolution is obtained by means of the ablation technique described in European Patent No 649374, wherein a driographic printing plate precursor is imaged digitally by means of an infra-red diode laser or a YAG laser, and the image is formed directly through the elimination of unwanted material. The technique involves exposing a plate precursor, incorporating an infra-red radiation abatable coating covered with a transparent cover sheet, by directing the beam from an infra-red laser at sequential areas of the coating so that the coating ablates and loses its ink repellancy in those areas to form an image, removing the cover sheet and ablation products, and inking the image.

A heat mode recording material is disclosed in US Patent No 4034183 which comprises an anodised aluminium support coated with a hydrophilic layer. On imagewise exposure using a laser, the exposed areas are rendered hydrophobic, and thereby accept ink.

Japanese patent application laid open to public inspection No 49-117102 (1974) discloses a method for producing printing plates wherein a metal is incorporated in the imaging layer of a printing plate precursor which is imaged by irradiation with a laser beam modulated by electric signals. Typically, the plate precursor comprises a metal base, such as aluminium, coated with a resin film, which is typically nitrocellulose, and on top of which has been provided a thin layer of copper. The resin and metal layers are removed in the laser-struck areas, thereby producing a printing plate. The disadvantage of this system, however, is that two types of laser beam irradiation are required in order to remove firstly the copper (eg by means of an argon-ion laser) and then the resin (eg with a carbon dioxide laser); hence, the necessary equipment is expensive.

Subsequently a method of printing plate production which obviated the requirement for a second laser exposure was disclosed in Japanese patent application laid open to public inspection No 52-37104 (1977). Thus, a printing plate precursor comprising a support, typically aluminium, an anodic aluminium oxide layer, and a layer of brass, silver, graphite or, preferably, copper is exposed to a laser beam of high energy density in order to render the exposed areas hydrophilic to yield a printing plate. The printing plate precursor is, however, of rather low sensitivity and requires the use of a high energy laser for exposure.

An alternative heat mode recording material for making a lithographic printing plate is disclosed in European Patent No 609941, which comprises a support having a hydrophilic surface, or provided with a hydrophilic layer, on which is coated a metallic layer, on top of which is a hydrophobic layer having a thickness of less than 50nm. A lithographic printing plate may be produced from the said material by imagewise exposing to actinic radiation, thereby rendering the exposed areas hydrophilic and repellent to greasy ink.

Conversely, European Patent No 628409 discloses a heat mode recording material for making a lithographic printing plate which comprises a support and a metallic layer, on top of which is provided a hydrophilic layer having a thickness of less than 50nm. A lithographic printing plate is produced by imagewise exposing the material to actinic radiation in order to render the exposed areas hydrophobic and receptive to greasy ink.

In each of the two foregoing heat mode recording materials, however, difficulties in printing will be encountered. On exposure of the materials to actinic radiation, the energy is converted to heat in the image areas by interaction with the metallic layer, thereby destroying the hydrophilicity or hydrophobicity - depending on the material employed - of the topmost layer in those areas. Consequently, the surface of the metallic layer becomes exposed, and the success of the printing operation is dependent upon differences in hydrophilicity and oleophilicity between the metallic surface and the hydrophilic or hydrophobic layer, as the case may be. Since the metallic layer functions as the hydrophobic surface in one case, and as the hydrophilic surface in the alternative case, it would be expected that such differences in hydrophilicity and oleophilicity would not be sufficiently clearly defined so as to provide a satisfactory printing surface. Furthermore, when a hydrophilic layer is present, and the metallic surface functions as the oleophilic areas of the plate, image areas will necessarily be printed from the metallic surface; such an arrangement is known to be unsatisfactory, and to result in difficulties in achieving acceptable printing quality.

It is an object of the present invention to provide a lithographic printing plate having excellent printing properties, and a method of making said plate which obviates the requirement for the use of processing developers after exposure.

It is a further object of the present invention to provide a method of preparing a lithographic printing plate which does not require the use of costly intermediate film and relies on direct-to-plate exposure techniques.

It is a still further object of the present invention to provide a method of producing a lithographic printing plate in which a high quality image results from the ablation of a metallic layer from a hydrophilic support, thus providing a high degree of differentiation between hydrophilic and oleophilic areas.

In the case of the present invention, a metallic layer is applied to a substrate by means of an electroless deposition process. The resulting layer is then imagewise exposed to a beam of high intensity laser radiation, causing the metal in the radiation-struck areas to be physically activated and removed from the substrate, leaving a positive image of the original on the substrate.

According to the present invention there is provided a method of preparing a lithographic printing plate, said method comprising:

(a) providing a lithographic printing plate precursor comprising:

(i) a grained and anodised aluminium substrate having coated thereon

(ii) a metallic layer deposited by means of an electroless deposition process; and

(b) imagewise exposing said precursor by means of a high intensity laser beam.

The aluminium substrate is electrochemically grained with an alternating electric current in a bath containing mineral or organic acids, or their mixtures, to give a roughened surface with a Centre Line Average (CLA) of between 0.2 μm and 1.5 μm, preferably between 0.4 μm and 1.0 μm.

The grained aluminium is then chemically cleaned in either mineral acid or aqueous alkali to remove smut which may be present in the form of metal, metal oxides and metal hydroxides.

Subsequently, the aluminium is electrochemically anodised with a direct electric current in a bath containing mineral or organic acids, or their mixtures, to provide an aluminium oxide film with an anodic weight of between 1.5 g/m^2 and 6.0 g/m^2, preferably between 2.0 g/m^2 and 5.0 g/m^2. It is preferable that the said aluminium oxide film should be substantially porous, and that the pores should extend substantially from the aluminium/aluminium oxide interface to the surface of the substrate, such that in excess of 95% of the pores have a diameter which lies in the range between 5 nm and 100 nm. Optionally, the surface of the pores may be chemically treated in order to partly or completely seal the substrate.

The metallic layer is deposited on the grained and anodised aluminium surface to a coating weight of between 0.2 g/m^2 and 1.5 g/m^2, preferably between 0.3 g/m^2 and 1.2 g/m^2. At least 80% by weight of the metal is deposited as colloidal particles having a diameter which lies in the range of from 10 nm to 300 nm, preferably from 50 nm to 200 nm.

In order to increase the adhesive force between the metal and the aluminium oxide film such that the metal remains adhered to the substrate during the lithographic printing process, the grained and anodised aluminium substrate is dipped into an aqueous colloidal dispersion of a metal or metal sulphide such that the colloidal metal or metal sulphide is adsorbed by the substrate to a weight of between 0.01 mg/m^2 to 100 mg/m^2, preferably between 0.1 mg/m^2 and 10 mg/m^2. Preferably, the aqueous colloidal dispersion of a metal or metal sulphide is stabilised with a polymeric material containing acid or acid salt functionalities.

A preferred method of obtaining a metallic layer is by dipping the grained and anodised aluminium substrate which has an adsorbed colloidal dispersion of metal or metal sulphide into a stabilised ionic solution of the metal and a reducing agent. The resulting metallic layer is well adhered.

The metallic layer may contain impurities of metal sulphide or oxide of up to 10% and preferably of at least 0.1%.

Preferably, in the case of the present invention, the metallic layer is silver and the silver layer is applied to a substrate comprising grained and anodised aluminium by means of electroless deposition according to the silver salt diffusion transfer process.

In the diffusion transfer process, a silver halide emulsion layer is transformed, by treatment with a so-called silver halide solvent, into soluble silver complex compounds which are then allowed to diffuse into an image receiving layer and are reduced therein by means of a developing agent, generally in the presence of physical development nuclei, to form a metallic silver layer.

Two such systems are available: a two sheet system in which a silver halide emulsion layer is provided on one element and a physical development nuclei layer is provided on a second element, the two elements are placed in contact in the presence of developing agent(s) and silver halide solvent(s) in the presence of an alkaline processing liquid, and subsequently peeled apart to provide a metallic silver layer on the second element; and a single sheet system wherein the element is provided with a physical development nuclei layer, a silver halide emulsion layer is provided on top thereof, the element is treated with developing agent(s) and silver halide solvent(s) in the presence of an alkaline processing liquid, and the element is washed to remove spent emulsion layer and leave a metallic silver layer which is formed in the layer containing physical development nuclei.

Alternatively, the diffusion transfer process may be used to apply a metallic silver layer by overall exposing a positive working silver halide emulsion layer to form a latent negative image which is then developed in contact with a physical development nuclei layer to form a metallic silver layer. Again, the process may be carried out using either a single sheet or a double sheet system.

Preferably, the present invention utilises a single sheet system in which a coating comprising a silver halide in a suitable binder resin, such as gelatin, is coated on to a grained and anodised aluminium substrate which has an adsorbed colloidal dispersion of silver or other metal or metal sulphide. The assembly is then treated with a solution containing a silver halide ligand such as a thiosulphate or thiocyanate salt to form a complex which is then catalytically reduced by interaction with the adsorbed silver or other metal or metal sulphide via the application of an organic reducing agent, such as hydroquinone or a salt of ascorbic acid.

The principles of the silver complex diffusion transfer process are fully described in the publication "Photographic Silver Halide Diffusion Processes" by Andre Rott and Edith Weyde, The Focal Press, London and New York, 1972, and further detail may be gleaned by reference thereto.

In order to prepare a lithographic printing plate, the precursor is imaged by a beam of radiation, preferably from a laser operating in the infra-red region of the spectrum. Examples of suitable infra-red lasers include semiconductor lasers and YAG lasers, for example the Gerber Crescent 42T Platesetter with a 10W YAG laser outputting at 1064 nm. Exposure to the beam of radiation causes ablation of the metallic layer to occur in the radiation-struck areas.

It is necessary that the silver or other metal which is deposited by means of an electroless deposition process should absorb at least 5%, and preferably at least 30%, of the energy of the incident beam of laser radiation.

It is also a requirement that at least 90%, and preferably at least 95%, of the silver or other metal which is struck by the laser radiation in the imagewise exposed areas should be removed by the action of the radiation.

Prior to, or following exposure, the plate is preferably prepared for printing operations by treatment with a composition comprising a proteolytic enzyme, a silver oleophilising agent and a desensitising compound. In this way, it is possible to ensure good ink acceptance in image areas and a high degree of hydrophilicity in background areas, thus enabling a good start-up on press to be achieved.

Suitable enzymes for use in the above composition may include, for example, trypsin, pepsin, ficin, papain or the bacterial proteases or proteinases. Oleophilising compounds may be chosen from those disclosed on pages 105 to 106 of "Photographic Silver Halide Diffusion Processes" by Andre Rott and Edith Weyde, but mercapto compounds and cationic surfactants such as quaternary ammonium compounds are of particular value. Carbohydrates such as gum arabic, dextrin and inorganic polyphosphates such as sodium hexametaphosphate provide useful desensitising compounds in these compositions.

Typically, the compositions comprise aqueous solutions containing from 0.1% to 10.0% by weight of enzyme, from 0.05% to 5.0% by weight of oleophilising compound and from 1.0% to 10.0% by weight of desensitising compound.

The method of the present invention provides press ready plates showing high image quality, good press properties and high durability on press without the requirement for the use of costly intermediate film and developer chemistry, and the attendant inconvenience resulting from the use of these materials.

The following examples are illustrative of the invention, without placing any limit on the scope thereof :

EXAMPLES

Plate A

A sheet of aluminium was degreased in a 5% w/w aqueous solution of sodium hydroxide before being electrochemically grained with an alternating electric current in a mixture of acetic and hydrochloric acids according to the method disclosed in British Patent No. 1598701, then cleaned with a 10% aqueous solution of phosphoric acid and finally anodised with a direct electric current in sulphuric acid.

The sheet was rinsed with water to remove residual acid and a Carey Lea colloidal dispersion of silver stabilised with ammonium polyacrylate was applied to the grained and anodised surface to give a coating weight of 1 mg/m^2 of silver, and this was then further coated with a gelatino-silver chlorobromide dispersion to give a coating weight of 4 g/m^2 and a silver coating weight of 1.6 g/m^2.

A diffusion transfer developer was prepared comprising an aqueous solution containing 11% w/w sodium sulphite, 2% w/w hydroquinone, 0.6% w/w Phenidone (1-phenyl-3-pyrazolidone), 1% w/w sodium thiosulphate and 3% w/w 2-methylaminoethanol. The pH of the developer solution was adjusted to 12 by the addition of sodium hydroxide.

The above plate precursor was dipped into the developer at 20 °C for 20 seconds, and then rinsed with warm water to remove residual coating and leave a physically developed silver layer on a grained and anodised aluminium substrate.

The resulting assembly was loaded onto a Gerber Crescent 42T internal drum Laser Platesetter fitted with an extraction system comprising a curved nozzle about 1cm from the surface of the plate, an air suction pump and a 0.3 μm HEPA filter for removal of ablation debris and imagewise exposed to a 10W YAG laser outputting at a wavelength of 1064 nm and delivering a power density of 8 MW/cm^2 to ablatively remove the silver in the background areas and thereby create an image.

After exposure, the surface of the printing plate was treated with an aqueous solution comprising a proteolytic enzyme, an oleophilising agent and a desensitising gum prior to mounting on a printing press in order to ensure a good start-up to printing operations with image areas showing high oleophilicity and background non-image areas being clean and free from ink adhesion. The plates were mounted on a Drent Web Offset Printing press and the number of good copies produced during the print run was recorded.

Plate B

A sheet of aluminium was degreased, grained and cleaned as described for Plate A, and then anodised with a direct electric current in a mixture of sulphuric and phosphoric acids.

The sheet was rinsed with water to remove residual acid and a Carey Lea colloidal dispersion of silver was applied to the grained and anodised surface to give a coating weight of 1 mg/m^2 of silver.

The resulting assembly was dipped for 60 seconds in an aqueous solution containing 2.8% w/w ferrous sulphate pentahydrate, 1.6% w/w ferric nitrate nonahydrate, 4.0% w/w citric acid, 0.0008% w/w oleylamine, 0.0008% w/w acetic acid, 0.0016% w/w Triton X102® (a commercial non-ionic surfactant) and 1% w/w silver nitrate at 20 °C.

The resulting printing plate precursor, comprising a silver layer applied by electroless deposition on to a grained and anodised aluminium substrate, was exposed and finished in the same way as for Plate A, then mounted on a Drent Web Offset Printing press, and the number of good copies produced during the print run was recorded.

Plate C

A sheet of grained and anodised aluminium substrate was prepared as described for Plate A.

A silver layer was vacuum deposited on the grained and anodised surface by a sputtering technique to give a shiny, non-colloidal silver layer having a coating weight of 0.5 g/m^2.

The plate was exposed and finished in the same way as for Plate A, then mounted on a Drent Web Offset Printing press, and the number of good copies produced during the print run was recorded.

Plate D

A sheet of grained and anodised aluminium substrate was prepared as described for Plate A.

The sheet was rinsed with water to remove residual acid and then coated with a gelatino-silver chlorobromide dispersion to give a coating weight of 4 g/m^2 and a silver coating weight of 1.6 g/m^2.

The resulting plate precursor was processed in a diffusion transfer developer and subsequently exposed and finished, in the same way as previously described for Plate A. The plate was mounted on a Drent Web Offset Printing press, and the number of good copies produced during the print run was recorded.

Plate E

A sheet of aluminium was degreased in a 5% aqueous solution of sodium hydroxide before being cleaned with a 10% aqueous solution of phosphoric acid and anodised with a direct electric current in sulphuric acid.

The resulting anodised aluminium substrate was rinsed, then coated with a Carey Lea colloidal dispersion of silver and a gelatino-silver chlorobromide dispersion, and finally processed through a diffusion transfer developer in the same way as described for Plate A in order to prepare a lithographic printing plate precursor.

The printing plate precursor was exposed and finished as described for Plate A, then mounted on a Drent Web Offset Printing press, and the number of good copies produced during the print run was recorded.

Plate F

A sheet of aluminium was degreased in a 50% w/w aqueous solution of sodium hydroxide before being electrochemically grained with an alternating electric current in a mixture of acetic and hydrochloric acids according to the method disclosed in British Patent No. 1598701, and then cleaned with a 10% aqueous solution of phosphoric acid.

The resulting grained aluminium substrate was rinsed, then coated with a Carey Lea colloidal dispersion of silver and a gelatino-silver chlorobromide dispersion, and finally processed through a diffusion transfer developer in the same way as described for Plate A in order to prepare a lithographic printing plate precursor.

The printing plate precursor was exposed and finished as described for Plate A, then mounted on a Drent Web Offset Printing press, and the number of good copies produced during the print run was recorded.

Plate G

A sheet of grained and anodised aluminium substrate was prepared as described for Plate B.

The sheet was rinsed with water to remove residual acid and a Carey Lea colloidal dispersion of silver was applied to the grained and anodised surface to give a coating weight of 1 mg/m^2 of silver. The resulting assembly was dipped for 5 minutes at 20°C in an aqueous solution having a formulation as described for Plate B.

The resulting printing plate precursor, comprising a silver layer applied by electroless deposition onto a grained and anodised aluminium substrate, was exposed and finished in the same way as for Plate A, then mounted on a Drent Web Offset Printing press, and the number of good copies produced during the print run was recorded.

The results of the tests are shown in Table 1.

Plate Sample	Silver wt (g/m^2)	Approx Average silver particle size (nm)	CLA (μm)	Anodic weight (g/m^2)	Anodic pore diameter (nm)	% Absorption at 1064 nm	% Silver removal by laser radiation in exposed areas	Press durability (approx no of copies)
A	0.6	150	0.6	4.2	7	32	99	90000
B	0.7	200	0.6	3.1	30	25	92	90000
C	0.5	1000	0.6	4.2	7	2	20	no prints
D	0.4	150	0.6	4.2	7	20	99	1000
E	0.5	>300	0.15	4.2	7	15	50	100
F	0.5	100	0.6	0.0	n/a	10	30	no prints
G	2.3	>300	0.6	3.1	30	20	30	no prints

TABLE 1

CLAIMS

1. A method of preparing a lithographic printing plate, said method comprising :

   (a) providing a lithographic printing plate precursor comprising :

      (i) a grained and anodised aluminium substrate having coated thereon

      (ii) a metallic layer deposited by means of an electroless deposition process ; and

   (b) imagewise exposing said precursor by means of a high intensity laser beam.

2. A method as defined in claim 1 wherein said grained and anodised aluminium substrate is treated with an aqueous colloidal dispersion of a metal or metal sulphide, prior to application of the metallic layer, such that said colloidal metal or metal sulphide is adsorbed by said substrate to a weight of between $0.01 mg/m^2$ and $100 mg/m^2$.

3. A method as defined in claim 2 wherein said metallic layer is applied by dipping said treated substrate into a stabilised ionic solution of a metal and a reducing agent.

4. A method as defined in claims 1-3 wherein said metallic layer is deposited on said grained and anodised aluminium substrate to a coating weight of between $0.2 g/m^2$ and $1.5 g/m^2$, at least 80% of said metal being in the form of colloidal particles having a diameter lying in the range of from 10 nm to 300 nm.

5. A method as defined in claims 1-4 wherein said aluminium substrate is electrochemically grained with an alternating electric current in a bath containing mineral or organic acids or their mixtures to give a roughened surface with a Centre Line Average of between 0.2 μm and 1.5 μm.

6. A method as defined in claim 5 wherein said grained aluminium is chemically cleaned by treatment with either mineral acid or aqueous alkali to remove smut.

7. A method as defined in claim 5 or 6 wherein said grained aluminium is electrochemically anodised with a direct electric current in a bath containing mineral or organic acids or their mixtures to provide an aluminium oxide film having an anodic weight of between 1.5 g/m^2 and 6.0 g/m^2.

8. A method as defined in claims 1-7 wherein said metallic layer comprises a silver layer.

9. A method as defined in claims 1, 2 or 4-7 wherein said metallic layer comprises a silver layer, and wherein said silver layer is applied to said substrate by means of the silver salt diffusion transfer process.

10. A method as defined in claim 9 wherein said silver salt diffusion transfer process comprises a single sheet system wherein a coating comprising a silver halide and a gelatin binder resin is coated on to said substrate having an adsorbed colloidal dispersion of silver or other metal or metal sulphide, said assembly is treated with a solution containing a thiosulphate or thiocyanate salt acting as silver halide ligand, and the thus formed complex is catalytically reduced by interaction with the adsorbed silver or other metal or metal sulphide via the application of an organic reducing agent.

11. A method as defined in claims 8-10 wherein, prior to or following said imagewise exposure, said plate precursor or plate is treated with a solution comprising a proteolytic enzyme, a silver oleophilising agent and a desensitising compound.

12. A method as defined in claims 1-11 wherein said imagewise exposure of said lithographic printing plate precursor is effected by means of an infra-red laser which causes removal of at least 90% of the silver or other metal which is struck by the radiation in the imagewise exposed areas.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/03483

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41N1/08 B41C1/10 B41N3/03 B41N1/10

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)
IPC 6 B41N B41C G03F B41M

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Section Ch, Week 7718 Derwent Publications Ltd., London, GB; Class A97, AN 77-31738Y XP002080050 & JP 52 037104 A (FUJI PHOTO FILM CO LTD) , 22 March 1977 cited in the application see abstract ---	1-10,12
Y	EP 0 380 073 A (CIBA GEIGY AG) 1 August 1990 see column 4, line 53 - column 5, line 7; claims 1,5,9,14 --- -/--	1-8

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
3 November 1998	13/11/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rasschaert, A

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INTERNATIONAL SEARCH REPORT

International Application No
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