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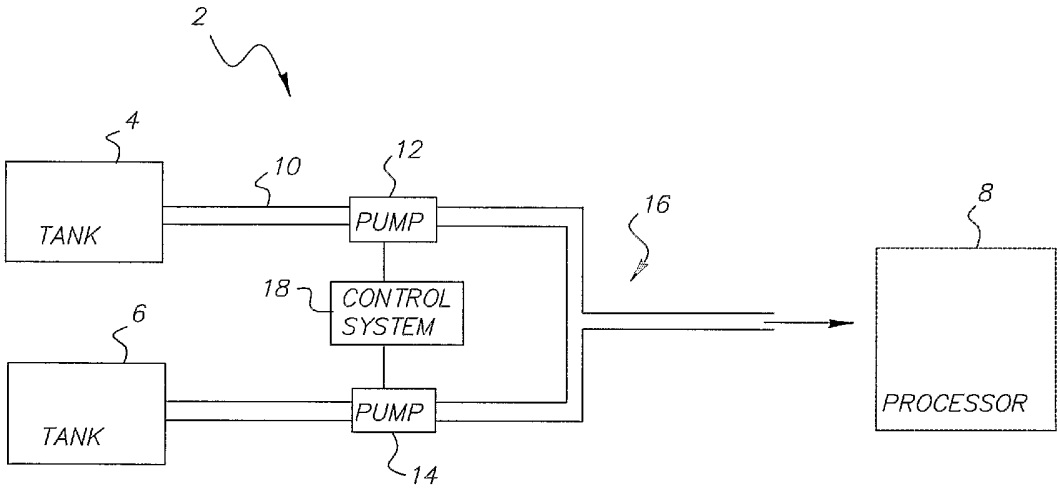
(54) Title: PHOTOGRAPHIC PROCESSING



(57) Abstract: The invention provides a method of redox photographic processing comprising the steps of processing photographic material in a processor using a developer solution and an amplifier solution or a developer/amplifier solution and then washing the processor using a cleaning solution. The cleaning solution for washing the processor comprises the amplifier solution or a constituent part of the developer/amplifier solution. The invention also provides a redox photographic processor. The processor has a processing chamber and a first storage tank for storing a developer solution and a second storage tank for storing an amplifier solution. The processor includes a control system to control provision of developer solution and amplifier solution to the processing chamber, the control system also functioning to control washing of the processor using the amplifier solution.

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PHOTOGRAPHIC PROCESSING

FIELD OF THE INVENTION

The present invention relates to photographic processing and in particular to a method of redox photographic processing in a single use processor i.e. a processor in which small volumes of processing solutions are used and discarded after a single use. The invention also relates to a redox photographic processor and control system for use with the processor to implement the method of the present invention.

BACKGROUND OF THE INVENTION

Redox amplification processes have been described, for example in United Kingdom Patent Numbers 1,268,126; 1,399,481; 1,403,418; and 1,560,572. In such processes colour materials are developed to produce a silver image (which may contain only small amounts of silver) and treated with a redox amplifying solution (or a combined developer/amplifier) to form a dye image.

The developer-amplifier solution contains a colour developing agent and an oxidising agent which will oxidise the colour developing agent in the presence of the silver image which acts as a catalyst.

Oxidised colour developer reacts with a colour coupler to form the dye image. The amount of dye formed depends on the time of treatment or the availability of the colour coupler and is less dependant on the amount of silver in the image than is the case in conventional colour development processes. This enables the amount of silver in photographic material to be processed to be correspondingly reduced without any expected reduction in image density.

Examples of suitable oxidising agents include peroxy compounds including hydrogen peroxide and compounds which provide hydrogen peroxide, e.g. addition compounds of hydrogen peroxide such as perborates and addition compounds of hydrogen peroxide with urea. Other oxidizing agents include cobalt (III) complexes including cobalt hexammine complexes; and periodates. Mixtures of such compounds can also be used.

In colour photography development (whether redox or conventional) it is necessary at an appropriate stage to remove the silver image which, if left behind would darken the dye image. Also it is necessary to remove unused silver halide because it darkens on exposure to light. To remove the silver the practice has been to convert the silver to silver halide with a suitable oxidizing agent known in the art as a bleach and then remove the silver halide with a fixing agent.

Suitable oxidizing agents are potassium ferricyanide, or ferric iron complexed with ethylenediaminetetraacetic acid acting in the presence of potassium bromide. The two steps may be combined using a solution called a bleach-fix or blix.

In the case of a bleach-fix employed after a redox amplification the solution only needs small amounts of iron (III) and thiosulphate because there is usually only a small amount of silver to remove.

Single use processors need washing between each process to remove the chemistry of the last step of the process. Low volume processors, such as the one described in PCT GB 2002/004141 are designed to process a length of material and then be washed out when no further processing is envisaged, for example after a certain delay in between orders. The washing of the processor ensures that no chemistry is left in the processor that might affect the next process cycle. It also removes any potential for the crystallisation of deposits on the processor parts. Usually water is used to carry out this washing or cleaning.

The wash, or cleaning, solution has to be supplied to the processor, either directly from a convenient water supply should it be available or from an additional tank in the processor. The latter takes up valuable space in the processor and requires some associated ancillary equipment such as pumps and level detectors to pump the solution into the machine. The volume of this extra tank can be minimised by using counter current machine washing, as described in GB 0204528.4, but still has to form part of the processing apparatus.

When water that might be used to clean a processor is stored it has a tendency to grow algae and bacteria, particularly if it is in the light and kept warm near to the warm tanks of the processor. This can be alleviated with the incorporation of a biocide into the water.

PROBLEM TO BE SOLVED BY THE INVENTION

A method of redox photographic processing is required which enables a reduction in the number of supply tanks and ancillary equipment such as pumps etc.

The invention further aims to provide a cleaning solution for cleaning a processor used in redox photographic processing which leaves no solid residue in the processor and in which growth of algae and bacteria is inhibited during storage.

A processor and control system for redox photographic processing is also required that relies on a reduced number of supply tanks and ancillary equipment such as pumps etc.

SUMMARY OF THE INVENTION

According to a first aspect of the present invention, there is provided a method of redox photographic processing. The method comprises the steps of processing photographic material in a processor using a developer solution and an amplifier solution or a developer/amplifier solution; and then, washing the processor using a cleaning solution, in which the cleaning solution for washing the processor comprises the amplifier solution or a constituent part of the developer/amplifier solution.

Preferably, the amplifier solution or the constituent part of the developer/amplifier solution used to wash the processor includes hydrogen peroxide or a compound capable of providing hydrogen peroxide.

According to a second aspect of the present invention, there is provided a redox photographic processor. The processor comprises a processing chamber and first and second storage tanks for processing solutions. In particular, the processor comprises a first storage tank for storing a developer solution and a second storage tank for storing an amplifier solution. A control system is also provided to control provision of developer solution and amplifier solution to the processing chamber, the control system also functioning to control washing of the processor using the amplifier solution.

In one example, the control system is a computer, programmed to control the processor to provide in a first step both developer solution and amplifier solution to the processor to develop photographic material using a redox amplification process and in a second step to provide amplifier solution to the processor to wash the processor.

ADVANTAGEOUS EFFECT OF THE INVENTION

The method of the present invention reduces the number of processing tanks in a redox photographic processor. The invention enables the use of the same solution that is used to convert a conventional colour developer into a redox developer/amplifier solution as a solution to wash the processor between processing stages or after processing. The footprint of the processor can therefore be reduced since no storage tank is required for storing processor wash solution.

Furthermore, the problem of growth of algae and bacteria in the wash solution storage tank is addressed since the oxidising agent functions also as a biocide.

In the case where a solution of hydrogen peroxide or compounds which provide hydrogen peroxide, e.g. addition compounds of hydrogen peroxide such as perborates and addition compounds of hydrogen peroxide with urea is used as the wash solution, this is particularly advantageous since it is environmentally benign converting to water on reaction with colour developer or by decomposition.

The amplifier solution which is also used as the wash solution for the processor can be added to the developer immediately prior to processing to make what is known in the art as a developer/amplifier or 'devamp' solution or alternatively it can be added separately to the processor after or during addition of the developer. In other words it is possible that a development step is used prior to the redox devamp step.

BRIEF DESCRIPTION OF THE DRAWINGS

Examples of the present invention will now be described in detail with reference to the accompanying drawings, in which:

Figure 1 shows a schematic representation of a photographic processor according to the present invention; and,

Figure 2 shows a graph of the sensitometric results achieved using the processing method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 shows a schematic representation of a photographic processor for redox processing of photographic material according to the present invention. The processor includes a solution supply system 2 having a number of storage tanks 4, 6 in which processing solution is stored. The system 2 includes a developer storage tank 4 and an amplification solution storage tank 6. The storage tanks are coupled to the processing chamber of a processor 8 via tubing 10 and supply pumps 12 and 14. In the example shown the output of tanks 4 and 6 is mixed prior to addition to the processor 8 with the use of a Y-Junction 16. The Y-junction functions as a mixing means having a dedicated input connected to each of the first and second storage tanks and a dedicated output connected to the processor. Alternative mixing means could be used. For example static mixers could be used or an additional chamber could be provided between the storage tanks and the processing chamber in which mixing takes place prior to solution being provided to the processor 8.

A control system 18 is provided to control operation of the pumps 12 and 14 and thereby control supply of solutions from the tanks 4 and 6 to the processing chamber of the processor 8. A single control system can be used for both pumps or alternatively a separate dedicated control system can be provided for each of the pumps 12 and 14.

Any suitable pumps may be used to pump the solutions from the tanks 4 and 6 to the processor 8. Examples include peristaltic pumps in combination with valves such as solenoid valves. The control system 18 used to operate the pumps or valves where peristaltic pumps are used may be any suitable type of control system. It could for example be a dedicated computer running under the operation of software. Alternatively it could be a microprocessor being configured to control operation of the pumps in accordance with a stored algorithm.

A preferred oxidising agent for use as the cleaning solution for the processor is hydrogen peroxide or a compound that provides hydrogen peroxide. Alternatives include amongst others, Fremy's salt $K_4[ON(SO_3)_2]_2$, persulfate and peroxides including organic peroxides.

According to the present invention, the amplification solution is also used as a cleaning solution to clean the processor. This has the advantage that a separate storage tank for a cleaning solution is not required. Additionally since the amplification solution is usually biocidal, the growth of algae and bacteria in the tank is avoided.

In the example shown in Figure 1, a separate processor is used for the developer or developer/amplification stage of the processing and so the only solutions coupled to the processor are the developer solution and the amplifier solution. It is also possible that further steps of the processing could take place in the same tank. In this case further storage tanks would be required to provide solutions such as bleach, bleach-fix, wash solution for the photographic material and any other that may be required although the solution used to wash the processor may also be used to wash the processed photographic material.

The present invention is particularly useful to low volume single use processors i.e. processors in which a small volume of processing solution is used to exhaustion and then discarded after use. Examples include the low volume processor, described in PCT GB 2002/004141 which is designed to process a length of material and then be washed out when no further processing is envisaged, for example after a certain delay in between orders.

The cleaning solution supplied from tank 6 may also be used to wash the photographic material as well as to wash the processor.

EXAMPLE

This example sets out to demonstrate the invention using an amplifier/cleaning solution to make a developer/amplifier.

The experiment was carried out in Shallow Tray processor as described in International Patent Application Number PCT/GB2002/004141. It was built with a 4inch (10.2cm) tray width with two consecutive trays – one for developer and

one for bleach-fix. Washing after the bleach-fix was by means of a felt inclined plane ramp, described in UK Patent Application Number GB0204528.4. The bleach-fix tray was fitted with a replenishment pump and a drain pump. The developer tray was fitted with two replenishment pumps, one supplying replenisher and one amplifier/cleaning solution, and a drain pump. Connectors (in this case tubes) coming from the developer replenishment pumps were connected to a Y-junction which was connected to the developer tray replenisher inlet. In this way the replenisher and amplifier/cleaning solutions were mixed before entering the developer tray. In other words a developer/amplifier solution was supplied to the processor.

The pump rates of the drain pumps were set to the sum of the replenishment pumps connected to the appropriate tray. Each tray could be charged by turning on the replenisher pumps only. During the processing operation the level in the tank was kept constant by adjusting the drain pumps to keep the amount of liquid in the tray constant.

The following solutions were used

Developer Replenisher

To make one litre

875g	water (demineralised)
33g	potassium carbonate
5g	DEHA
7.5g	CD3
10drops	Tween 80
1ml	Dequest 2010
2g	Blankophor REU

pH adjusted with 10% nitric acid to 10.5

Amplifier/Processor Cleaning solution

Three solutions were made up

1. demineralised water (comparison)
2. 0.3% hydrogen peroxide (invention)
3. 0.6% hydrogen peroxide (invention)

Bleach-fix

To make 1 litre

200 ml	1.56M ferric ammonium EDTA solution
140g	ammonium thiosulphate
20g	sodium hydrogen sulphite
10g	glacial acetic acid

pH adjusted to 6.0 with either ammonia solution or sulphuric acid

Paper Wash

Tap water to which was added 2g/l Silwet L-7607.

Strips of low silver colour print paper were exposed to a 21-step wedge with density increments at 1 centimetre intervals in a sensitometer.

Process	**Time (s)**	**Temperature (C)**	**Rep. Rate (ml/m^2)**
Developer/amplifier	40s	40	54/54
Bleach-Fix	38s	40	108
Wash	25	25	108

Before processing the process the processor was cleaned with 4 20ml changes of water in the counter-current mode discussed in UK Patent Application

Number GB0204528.4. The tray was drained of liquid and allowed to dry. No crystals were seen in the tray. To start the process 8mls water (Comparison) or amplifier/Processor Cleaning solution (Invention) was pumped into the developer tray, fed from the same storage bottle as the cleaning solution.

This was followed by pumping in 11ml developer replenisher and 11ml of amplifier/Processor Cleaning solution. 30ml bleach-fix replenisher was pumped into the bleach-fix tank. The mixture was stirred for about 15s by starting the agitation rollers at a rate of 1Hz. The replenisher pumps were started and a length of paper inserted in to the machine. The developer solution and amplifier solution pumps were set to pump 54ml/m^2 each and the bleach-fix pump was set to pump 108ml/m^2. This was carried out for both the comparison and inventions.

The processed strips were allowed to dry at room temperature and then the densities read with a densitometer at 1 cm intervals. The results of the experiment are shown in Figure 2.

The results show that the addition of the peroxide containing cleaning solution was able to cause amplification and to give reasonable sensitometry to a low silver paper.

CLAIMS:

1. A method of redox photographic processing comprising the steps of processing photographic material in a processor using a developer solution and an amplifier solution or a developer/amplifier solution; and then,

washing the processor using a cleaning solution, in which the cleaning solution for washing the processor comprises the amplifier solution or a constituent part of the developer/amplifier solution.

2. A method according to claim 1, in which the amplifier solution or the constituent part of the developer/amplifier solution used to wash the processor includes hydrogen peroxide or a compound capable of providing hydrogen peroxide.

3. A method according to claim 1, in which the amplifier solution or the constituent part of the developer/amplifier solution used to wash the processor includes $K_4[ON(SO_3)_2]_2$, persulfate and peroxides including organic peroxides

4. A method according to claim 1 in which a combined developer/amplifier solution is used, the solution comprising a colour developer solution and an amplifier solution the two components being mixed prior to introduction to the processor.

5. A method according to claim 1 in which a combined developer/amplifier solution is used, the solution comprising a colour developer solution and an amplifier solution the two components being mixed in the processor.

6. A redox photographic processor, comprising:

a processing chamber;

a first storage tank for storing a developer solution;

a second storage tank for storing an amplifier solution; and,

a control system to control provision of developer solution and amplifier solution to the processing chamber, the control system also functioning to control washing of the processor using the amplifier solution.

7. A processor according to claim 6, further comprising one or more pumps to pump solution from the first and second storage tanks to the processing chamber, wherein the control system is operative to control the pumps.

8. A processor according to claim 6, further comprising mixing means to enable mixing of the developer solution and amplifier solution prior to entry of the solutions to the processing chamber.

9. A processor according to claim 8, in which the mixing means comprises a Y-tube having a dedicated input connected to each of the first and second storage tanks and a dedicated output connected to the processing chamber.

10. A processor according to claim 6, in which the control system is a computer, programmed to control the processor to provide in a first step both developer solution and amplifier solution to the processor to develop photographic material using a redox amplification process and in a second step to provide amplifier solution to the processor to wash the processor.

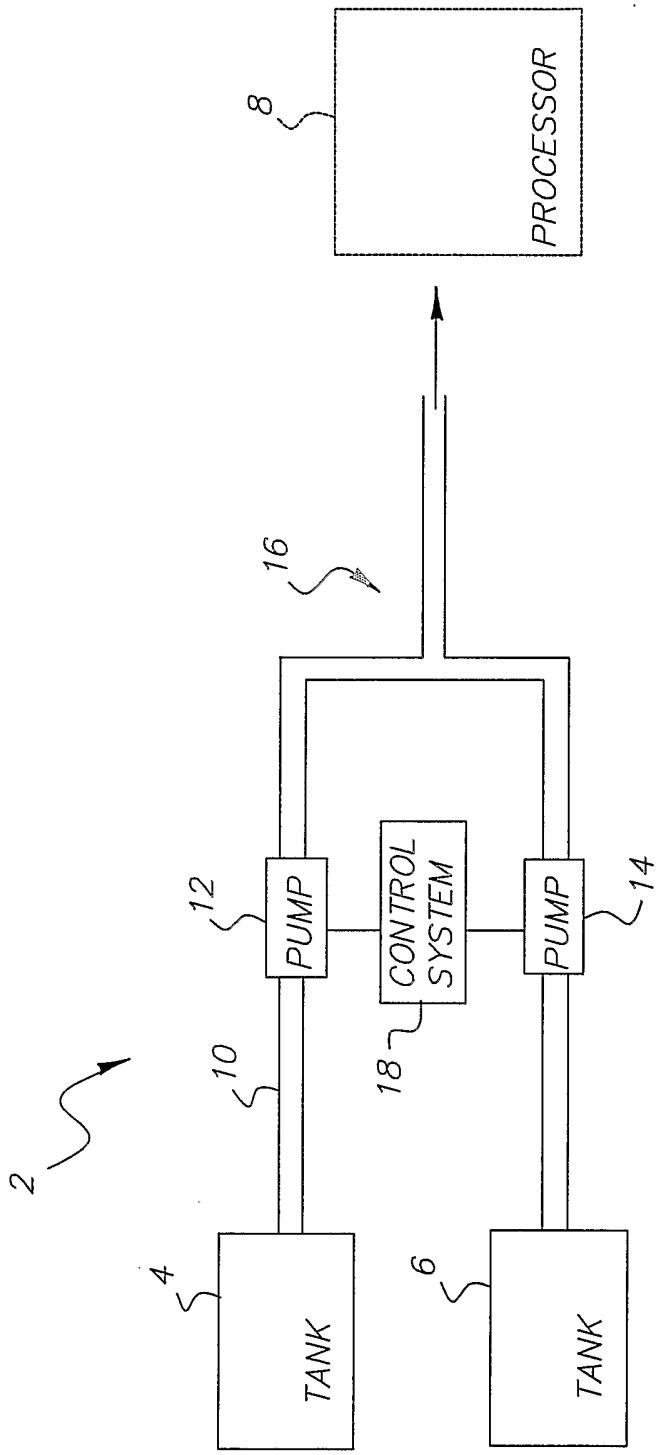
PROCESSOR
8
16
PUMP
12
CONTROL SYSTEM
18
PUMP
14
10
2
TANK
4
TANK
6

FIG. 1

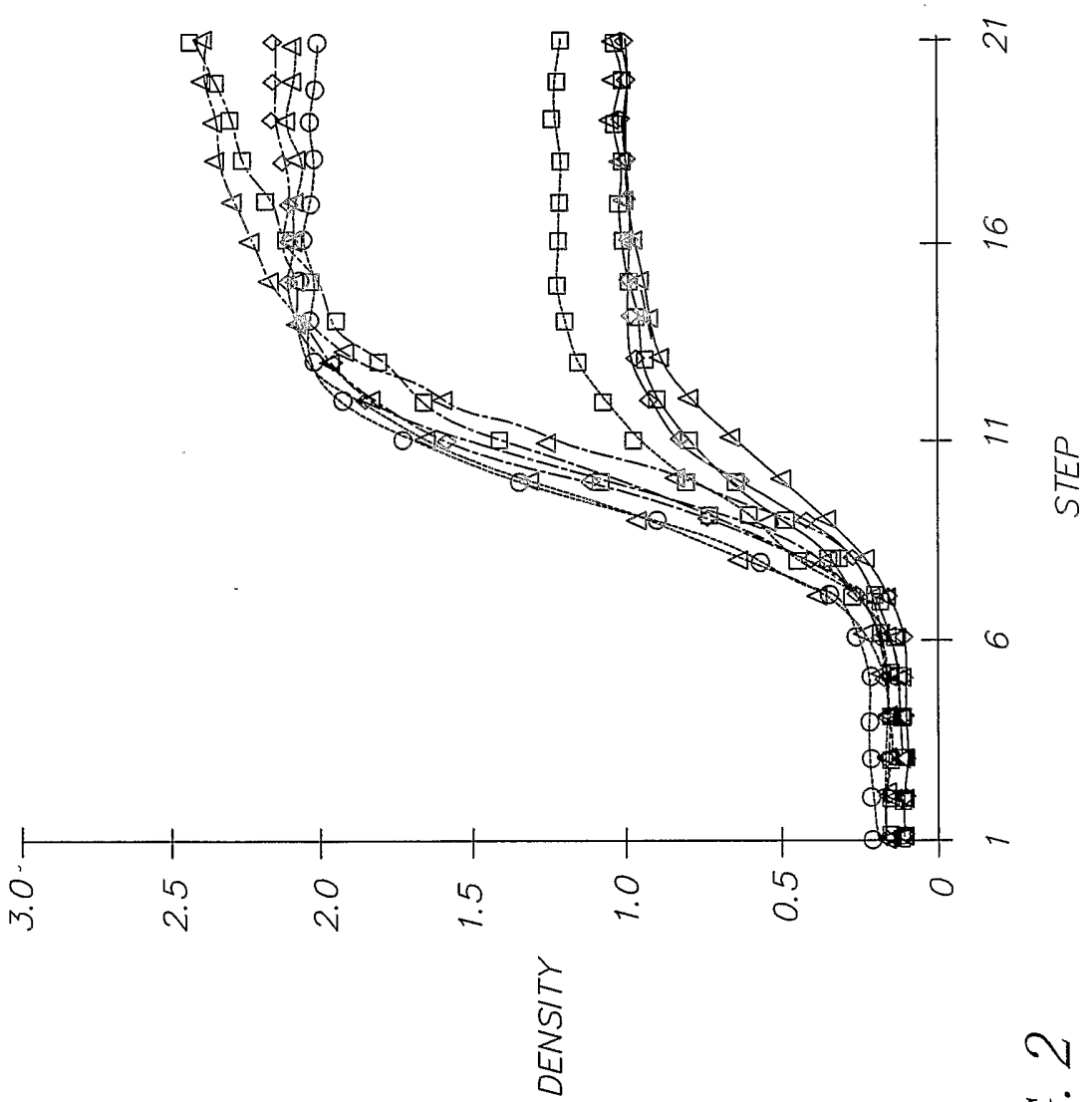
WATER RED
WATER GREEN
WATER BLUE
2% H2O2 RED
2% H2O2 GREEN
2% H2O2 BLUE
1% H2O2 RED
1% H2O2 GREEN
1% H2O2 BLUE
DENSITY
3.0
2.5
2.0
1.5
1.0
0.5
0
STEP
1
6
11
16
21

FIG. 2

INTERNATIONAL SEARCH REPORT

ıational Application No
.../GB2004/001046

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03C11/00 G03D3/06

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 7 G03C G03D

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 0 706 085 A (KODAK) 10 April 1996 (1996-04-10) page 5, line 13 - line 15 page 8, line 26 - line 28; claims 1-3	1 2-10
Y	EP 0 919 866 A (AGFA-GEVAERT) 2 June 1999 (1999-06-02) column 1, line 29 - line 48 column 2, line 3 - line 7 column 2, line 37 - line 42 column 3, line 1 - line 6 column 3, line 34 - line 48 column 5, line 31 - line 52; figure 1	2-10
Y	DE 40 25 021 A (HECKL) 13 February 1992 (1992-02-13) column 1, line 37 - line 48; claim 1	2,3,6

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 June 2004	15/06/2004

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	Magrizos, S

INTERNATIONAL SEARCH REPORT

ational Application No
PCT/GB2004/001046

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 54 065534 A (FUJI) 26 May 1979 (1979-05-26) claim 1	2,6
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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		DE 69024599 T2	13-06-1996
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