

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 837 364 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**22.04.1998 Bulletin 1998/17**

(51) Int Cl.<sup>6</sup>: **G03C 11/24**

(21) Application number: **97830513.4**

(22) Date of filing: **10.10.1997**

(84) Designated Contracting States:

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

Designated Extension States:

**AL LT LV RO SI**

(30) Priority: **15.10.1996 IT BO960515**

(71) Applicant: **Serf S.r.l.**

**40050 Argelato (Bologna) (IT)**

(72) Inventor: **Miciano, Marino**

**40137 Bologna (IT)**

(74) Representative: **Lanzoni, Luciano**

**c/o BUGNION S.p.A.**

**Via dei Mille, 19**

**40121 Bologna (IT)**

(54) **A process for the treatment and recovery of materials from the production and development of photographic and x-ray films**

(57) A process for the treatment and recovery of materials from the production and development of photographic and x-ray films. The process substantially includes the following operating stages: a first stage involving the shredding of the said materials; a second stage involving oxidation of the metallic silver to ionic

silver; a third stage for solubilization of the silver salt in water; a fourth stage for the recovery of the metallic silver; a fifth stage for solubilization of the gelatin in an alkaline bath; a sixth stage for recovery of the gelatin; a seventh stage involving the washing, rinsing and drying of the polyester; an eighth stage for drying the polyester.

**EP 0 837 364 A1**

## Description

The present invention relates to a process for the treatment and recovery of materials from the production and development of photographic and x-ray films. In particular, it relates to a process for the recovery, by means of chemical/physical treatments, of the materials of which photographic films and x-ray plates are made, more precisely the recovery of silver, polyester, which forms the base of the photo-x-ray film, and the animal gelatin which coats one or both surfaces of the aforementioned polyester base.

The present invention, therefore belongs to the sector of industrial chemical processes designed to recover materials which, when recycled, are suitable for further use.

As is known, the recovery of materials from the production and development of photographic and x-ray films currently regards only the metallic part (including the oxidised form) of the said films, that is to say, silver. Obviously, this is due to the intrinsic value of the said metal.

The rest, that is to say, the polyester and gelatin, is currently discarded, this being an undoubted disadvantage from the economic (and environmental) viewpoint, considered that recycled polyester and gelatin have excellent possibilities for re-use. For example, polyester in the textiles sector, and animal gelatin as feed for the bacterial flora in purification plant.

In accordance with conventional techniques, the silver may be recovered using dry or wet systems.

The dry system envisages that the starting material, i.e.: photosensitive plates or films, be subjected to combustion. In this case, the silver evaporates or remains as an unburned base body, which may then be gathered. In contrast, the polyester and gelatin are lost.

As is known, the wet system envisages the use of developing and fixing baths. The fixing bath is used to extract the "superfluous" silver from the fixed silver.

The object of the present invention is, therefore, to recover all of the material, that is to say, the silver, polyester and animal gelatin.

A further object is to effect the said recovery in a relatively simple, low cost manner. These objects, together with others, are all fulfilled by the process for the treatment and recovery of materials from the production and development of photographic and x-ray films, the main characteristics of said process being described in the claims herein. Further characteristics and advantages of the present invention are more clearly illustrated in the following description of the process, by way of example only, and not limited only to the sector protected by the present patent right.

The following is an example of the process.

The material to be treated consists of a base which is a polyester film, coated on one or both surfaces with a gelatin of animal origin, in which metallic silver or silver salt is dispersed.

The material normally arrives in bales of waste or sheets, not yet exposed, or in the form of x-ray plates in envelopes.

The first step, which is manual, consists in undoing the bales and separating the plates from the paper. The film is then shredded in a special machine and reduced to pieces whose size is 0.3 - 3 cm<sup>2</sup>. It is essential that the material be shredded, in order to allow the completion of the chemical reactions which must take place on both surfaces of the film. Larger dimensions would promote adhesion of the surfaces, preventing completion of the reactions and reducing the overall efficiency of the process. In particular, recovery of the silver would be compromised.

The material containing metallic silver is then subjected to a "bleaching" action, that is to say, oxidation of the metallic silver to ionic silver. This action occurs in an aqueous bath, kept at ambient temperature (10 - 25 °C), containing: copper sulphate (to oxidise the silver); hydrogen peroxide (to re-oxidise the copper); sodium chloride (to provide a counter-ion to the silver ion). The reaction occurs at pH 0.5 - 3. Lower pH values could cause the gelatin to be detached; whilst higher pH values would make the bleaching action less effective.

The treatment time varies from 3 to 15 minutes: lower times would be insufficient to complete the reaction; higher times could cause the gelatin to be detached.

The use of copper as an oxidising agent is determined by process economy and final quality of the polyester recovered: other oxidising agents would be more difficult to remove and would, as a result, pollute the final product. The following are the concentrations of the reagents: copper sulphate 5 - 12 %; sodium chloride 5 - 15 %; hydrogen peroxide 0.1 - 1 %.

The material containing bleached silver, that is to say, silver salt, is then treated in a fixing bath containing sodium thiosulphate. During this stage, the silver salt contained in the gelatin, and insoluble in water, is solubilized by the presence of the thiosulphate.

The reaction occurs at pH 4.5 - 5.5; lower pH values would render the thiosulphate unstable, whilst higher values would slow down the extraction-solubilization of the silver salt.

The treatment time is 3 - 15 minutes at a temperature of 10 - 25 °C; the concentration of the sodium thiosulphate may vary from 50 to 200 g/l. The fixing solution, enriched with silver, is then sent to the electrolytic recuperator; once the silver has been deposited, the bath is put into circulation again.

The material - now consisting of polyester coated with gelatin - is sent to the gelatin removal tank, which consists of a bath containing sodium hydrate 5 - 25 % and is kept at 55 - 80 °C. The gelatin solubilizing process occurs within 5 - 20 minutes.

The polyester is then sent to the washing, rinsing and centrifugation plant.

Afterwards, it is dried until the residual humidity is 0.1 - 3 % and packaged according to market require-

ments.

Obviously, the practical execution of the process in question may be subject to procedural variations, although these are all encompassed by the scope of the present patent.

In particular, product washing stages may be envisaged upstream of those operating stages which require unpolluted products from the operating stage upstream.

Moreover, all components may be substituted with technically equivalent parts to meet the various requirements.

## Claims

1. A process for the treatment and recovery of materials from the production and development of photographic and x-ray films, said materials substantially consisting in a polyester base, coated on one or both surfaces with a gelatin in which metallic silver or silver salt is dispersed, characterised in that the process includes the following operating stages:

- a first stage, involving shredding of the material into pieces with dimensions suitable for promoting the full efficiency of the said process;
- a second stage, involving oxidation of the metallic silver into ionic silver;
- a third stage, for solubilization of the silver salt in water;
- a fourth stage, for recovery of the metallic silver by means of electrolysis;
- a fifth stage, for solubilization of the gelatin in an alkaline bath;
- a sixth stage, for recovery of the gelatin;
- a seventh stage, involving washing, rinsing and drying of the polyester from which the silver and gelatin have been removed.

2. The process as described in claim 1, characterised in that it envisages an eighth stage, for drying the polyester until the residual humidity is between 0.1 and 3 %.

3. The process as described in claim 1, characterised in that the dimensions of the said pieces are between 0.3 and 3 cm<sup>2</sup>.

4. The process as described in claim 1, characterised in that the said oxidation of the metallic silver occurs in an aqueous bath containing: copper sulphate, to oxidise the metallic silver; hydrogen peroxide, to re-oxidise the copper, and sodium chloride, to provide a counter-ion to the silver ion; said oxidation occurring in accordance with the preset reaction parameters.

5. The process as described in claim 4, characterised

in that the reaction parameters are:  
reagent concentrations:

- copper sulphate: approx. 5 - 12 %;
- sodium chloride: approx. 5 - 15 %;
- hydrogen peroxide: approx. 0.1 - 1 %;
- pH values between approx. 0.5 and 3;
- treatment time between approx. 3 and 15 minutes;
- temperature between approx. 5 and 30 °C.

6. The process as described in claim 1, characterised in that the said solubilization of the silver salt occurs in an aqueous bath containing sodium thiosulphate, in accordance with the preset reaction parameters.

7. The process as described in claim 6, characterised in that the reaction parameters are:

- sodium thiosulphate concentration: approx. 50 - 200 g/l;
- pH values between approx. 4.5 and 5.5;
- treatment time between approx. 3 and 15 minutes;
- temperature between approx. 5 and 30 °C.

8. The process as described in claim 1, characterised in that the said solubilization of the gelatin occurs in an aqueous bath containing sodium hydrate, in accordance with the preset reaction parameters.

9. The process as described in claim 8, characterised in that the reaction parameters are:

- sodium hydrate concentration: approx. 5 - 25 %;
- pH values between approx. 13 and 14;
- treatment time between approx. 5 and 20 minutes;
- temperature between approx. 55 and 80 °C.

10. The process as described in claim 1, characterised in that the said washing and rinsing stage occurs in water, and the drying stage is effected by centrifugation.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 83 0513

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.6)
X	US 4 299 676 A (SKINNER JOHN H ET AL) 10 November 1981 * column 1, line 5 - column 2, line 54 * * column 5, line 44 - column 7, line 11 * ---	1,3-7	G03C11/24
A	US 5 418 115 A (TSUBAI YASUO ET AL) 23 May 1995 * column 6, line 17 - line 42 * * column 8, line 16 - line 62 * ---	1,4,5	
A	DATABASE WPI Section Ch, Week 7907 Derwent Publications Ltd., London, GB; Class E37, AN 79-12657B XP002052387 & JP 54 001 026 A (KONISHIROKU PHOTO IND CO LTD) , 6 January 1979 * abstract * ---	1,4,5	
A	DATABASE WPI Section Ch, Week 8747 Derwent Publications Ltd., London, GB; Class M14, AN 87-331438 XP002052388 & JP 62 237 447 A (MITSUBISHI PAPER MILLS LTD) , 17 October 1987 * abstract * ---	1,4,5	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US 3 793 168 A (LILLY R) * the whole document * ---	1,4-6	G03C C22B C25C C02F C08J
A	EP 0 239 805 A (FIXERSAVE LTD) 7 October 1987 * column 1, line 5 - column 2, line 18 * * column 4, line 1 - line 10 * --- -/--	1	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 19 January 1998	Examiner Lindner, T
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPC FORM 1503 03.82 (P04C01)



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 83 0513

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.6)
A	US 3 928 253 A (THORNTON J SCOTT ET AL) 23 December 1975 * column 1, line 34 - column 2, line 68 * * column 3, line 38 - column 4, line 15 * ---	1,8,9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	GB 1 432 000 A (HORIZONS RESEARCH INC) 14 April 1976 * page 1, line 11 - line 29 * * page 2, line 17 - line 69 * * page 4, line 42 - page 78 * * page 5, line 55 - line 68 * * page 5, line 115 - line 125 * ---	1-3,10	
A	US 3 647 422 A (WAINER EUGENE) 7 March 1972 * column 1, line 35 - line 43 * * column 1, line 62 - column 2, line 8 * * column 2, line 35 - line 62 * ---	1,2,8,9	
A	US 4 799 954 A (HOCHBERG JEROME) 24 January 1989 * column 3, line 7 - column 4, line 12 * ---	1-3,8,9	
A	US 3 047 435 A (WEMPLE RICHARD) 31 July 1962 * column 1, line 64 - column 2, line 32 * ---	1,8	
A	DATABASE WPI Section Ch, Week 7917 Derwent Publications Ltd., London, GB; Class G06, AN 79-33088B XP002052389 & SU 611 168 A (NONFER METALS HYDRO) , 15 May 1978 * abstract * --- -/--	1,8	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 19 January 1998	Examiner Lindner, T
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 82 (P04C01)



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 83 0513

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.6)
A	<p>DATABASE WPI Section Ch, Week 9228 Derwent Publications Ltd., London, GB; Class A23, AN 92-232294 XP002052390 &amp; SU 1 681 295 A (KAZAN CHEM PHOTO IND RES DES INST) , 30 September 1991 * abstract *</p> <p>---</p>	1,8,9	
A	<p>COOLEY A C: "SILVER RECOVERY FOR ENVIRONMENTAL COMPLIANCE IN PHOTOGRAPHIC PROCESSING" JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY, vol. 37, no. 4, 1 July 1993, pages 374-379, XP000423013 Chapter: Electrolytic Silver Recovery -----</p>	1	
The present search report has been drawn up for all claims			<p>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</p>
Place of search <b>MUNICH</b>		Date of completion of the search <b>19 January 1998</b>	Examiner <b>Lindner, T</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P04C01)