PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [5] : G03C 5/31	A1	**(11) International Publication Number:** WO 94/16362 **(43) International Publication Date:** 21 July 1994 (21.07.94)

(21) International Application Number: PCT/US93/10694

(22) International Filing Date: 12 November 1993 (12.11.93)

(30) Priority Data:
07/998,697 30 December 1992 (30.12.92) US

(71) Applicant: PFIZER INC. [US/US]; 235 East 42nd Street, New York, NY 10017 (US).

(72) Inventor: O'DONNELL, Alvin, John; 232 Waterman Avenue, North Providence, RI 02911 (US).

(74) Agents: RICHARDSON, Peter, C. et al.; Pfizer Inc., 235 East 42nd Street, New York, NY 10017 (US).

(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: RECOVERY OF ERYTHORBATES FROM PHOTOGRAPHIC SOLUTIONS

(57) Abstract

The present invention is directed to a method for the recovery of erythorbates from photographic solutions. In the disclosed method, the photographic solution is first acidified by passing it over an acidic cation exchange resin and the resultant solution is then passed over a weakly basic anion exchange resin.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

RECOVERY OF ERYTHORBATES FROM PHOTOGRAPHIC SOLUTIONS

The present invention is directed to a process for the recovery of erythorbate values from spent photographic solutions.

Typically, the processing of silver halide emulsions begins with the exposure of the emulsion to radiation to which the emulsion is sensitized to produce a latent image in the silver halide grains of the emulsion. The latent image is developed by immersion of the exposed emulsion in an aqueous developing solution usually containing a reducing agent which functions as a developer. An example of such a reducing agent is hydroquimone.

Other developing agents which have been used are derivatives of ascorbic acid, i.e. erythorbic acid or erythorbates. The use of these derivatives as developers are discussed in a number of United States Patents.

United States Patent Number 3,942,985 refers to a developer composition comprised of at least one iron chelate developer and ascorbic acid, or specific derivatives thereof.

United States Patent Number 2,688,549 refers to a photographic composition which uses ascorbic acid, and specified derivatives thereof, together with 3-pyrazolidone compounds as a developing medium.

United States Patent Number 3,022,168 refers to photographic developer compositions which use ascorbic acid as a developer. The compositions are at a pH of from about 8.5 to about 9.

United States Patent Number 5,098,819 refers to a photographic composition containing ascorbic acid; specified derivatives thereof, a sulfite, an alkali metal carbonate and a 3 pyrazolidone compound. The composition is at a pH of from 9.75 to 10.6.

In one embodiment the present invention is directed to a process for the substantial purification of the erythorbic values from a spent photographic solution containing said values comprising:

(a) acidifying a spent photographic solution containing said values by passing said solution over an acidic cation exchange resin;

(b) passing the acidified solution of (a) over a weakly basic anion exchange resin.

In a further embodiment, the process further comprises the step of (c) neutralizing the solution of (b) with a suitable base.

In a further embodiment, the process further comprises the step of recovering the erythorbic values from step (c).

Preferred is the process wherein said recovery is by crystallization.

Also preferred is a process wherein said crystallization is by the addition of a water miscible solvent.

Especially preferred is the process wherein said water miscible solvent is selected from the group consisting of aldehydes, ketones, and C_1-C_6 alkanols with an especially preferred alkanol being methanol.

Preferred is the process wherein said erythorbic values are erythorbates.

Also preferred is the process wherein said erythorbic values are erythorbic acid.

Preferred especially is the process wherein said acidic cation exchange resin is a sulfonic acid resin.

Also especially preferred is the process wherein said weakly basic anion exchange resin is an amine resin.

Preferred is the process wherein said base of step (c) is selected from the group consisting of alkali metal hydroxides and alkali metal carbonates; and mixtures thereof with an especially preferred alkali metal hydroxide being potassium hydroxide.

Further preferred is the process wherein said spent photographic solution is at a pH of from about 7.5 to about 11.0.

The process of the present invention is directed to the recovery of erythorbate values from spent photographic solutions. The photographic solution may contain erythorbic acid or salts thereof, for example, potassium erythorbate, as the sole developing agent. The photographic solution may contain alkyl esters of erythorbic acid, for example, methyl erythorbate, as the developing agent. The photographic solution may also contain any combination of erythorbic acid, salts thereof, or esters thereof.

The erythorbate values may be present as the sole developing agent in photographic compositions or may be in combination with other co-developing agents. Non limiting example of such other agents include alkali metal carbonates, for example, sodium carbonate and potassium carbonate; 3- pyrazolidone compounds such as phenidone (1 phenyl-3-pyrazolidone); alkali metal sulfites such as, for example, sodium

sulfite; metal chelating agents such as, for example, sodium ethylenediaminetetraacetic acid (EDTA); bromides such as, for example, potassium or sodium bromide; and organic antifogging agents such as tetrazoles. A typical photographic solution will contain any combination of the above listed components.

During the development of an image on a photographic medium, various components of the medium, notably the erythorbates, are converted to oxalic acids. Depending on the degree of decomposition, the spent photographic solution is normally at a pH of from about 7.5 to about 13.

In the first step of the process of the present invention, a spent photographic solution is acidified by passing over an acidic cation exchange resin, for example, a sulfonic acid type resin. An example of such a resin is Amberlite IRC-200 (Rohm and Haas, Philadelphia, PA) which is regenerated or activated with a mineral acid such as hydrochloric acid, sulfuric acid, phosphoric acid or nitric acid.

The acidified solution generated by passage through the acidic cation exchange resin is then passed over a weakly basic anion exchange resin, for example, an amine type resin. An example of such a resin is IRA-93 (Rohm and Haas, Philadelphia, PA). The resin may be activated by use of, for example, sodium hydroxide, potassium hydroxide or other bases, such as, for example, ammonium hydroxide.

After passage of the photographic solution over the weakly basic anion exchange resin, the solution may then be neutralized with an appropriate base. Non limiting examples of suitable bases which may be used are alkali metal hydroxides such as, for example, sodium hydroxide or potassium hydroxide, and alkali metal carbonates such as, for example, sodium carbonate or potassium carbonate. An especially preferred bases are sodium hydroxide and potassium hydroxide.

After the photographic solution has been neutralized, it may be used as is to reformulate fresh photographic developer solution.

Alternately, the solution may be concentrated by, for example, vacuum distillation. After concentration, the erythorbate values may be crystallized. Crystallization may be accomplished by cooling or by the addition of a water miscible solvent. Non limiting examples of water miscible solvents include aldehydes, ketones and lower (C_1-C_6) alkanols, for example, methanol.

Having described the invention in general terms, reference is now made to specific examples. It is to be understood that these examples are not meant to limit the present invention, the scope of which is determined by the appended claims.

EXAMPLE 1

One liter of spent photographic developing solution containing the equivalent of approximately 110 g. of erythorbic acid was acidified by passing it over an ion exchange column containing a cation exchange resin of the sulfonic acid type (e.g. Amberlite IRC-200) which had previously been put in the hydrogen form.

A portion of the resulting solution was then passed over a second ion-exchange column containing a weak basic anion exchange resin of the amine type (e.g. Amberlite IRA 93) which had previously been put in the free-base form.

A portion of that resulting solution was then neutralized with sodium hydroxide, concentrated by vacuum distillation and the sodium salt of erythorbic acid crystallized via the addition of methanol. After filtration, washing and drying the isolated salt exhibited a purity of 99.8% as determined by iodometric titration.

CLAIMS

1. A process for the substantial purification of the erythorbic values from a spent photographic solution containing said values comprising:

(a) acidifying a spent photographic solution containing said values by passing said solution over an acidic cation exchange resin;

(b) passing the acidified solution of (a) over a weakly basic anion exchange resin.

2. A process according to claim 1 further comprising the step of

(c) neutralizing the solution of (b) with a suitable base.

3. A process according to claim 1 further comprising the step of recovering the erythorbic values from step (b).

4. A process according to claim 2 further comprising the step of recovering the erythorbic values from step (c).

5. A process according to claim 3 wherein said recovery is by crystallization.

6. A process according to claim 4 wherein said recovery is by crystallization.

7. A process according to claim 5 wherein said crystallization is by the addition of a water miscible solvent.

8. A process according to claim 6 wherein said crystallization is by the addition of a water miscible solvent.

9. A process according to claim 7 when said water miscible solvent is selected from the group consisting of aldehydes, ketones, and C_1-C_6 alkanols.

10. A process according to claim 8 wherein said water miscible solvent is selected from the group consisting of aldehydes, ketones and C_1-C_6 alkanols.

11. A process according to claim 9 where said alkanol is methanol.

12. A process according to claim 10 wherein said alkanol is methanol.

13. A process according to claim 1 wherein said erythorbic values are erythorbic acid.

14. A process according to claim 1 wherein said erythorbic values are erythorbates.

15. A process according to claim 1 wherein said acidic cation exchange resin is a sulfonic acid resin.

16. A process according to claim 1 wherein said weakly basic anion exchange resin is an amine resin.

17. A process according to claim 2 wherein said base of (c) is selected from the group consisting of alkali metal hydroxides and alkali metal carbonates; and mixtures thereof.

18. A process according to claim 17 wherein said alkali metal hydroxide is selected from the group consisting of sodium hydroxide and potassium hydroxide.

19. A process according to claim 1 wherein said spent photographic solution is at a pH of from about 7.5 to about 11.0.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 93/10694

A. CLASSIFICATION OF SUBJECT MATTER

G 03 C 5/31

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)

G 03 C

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.
A	US, A, 5 098 819 (KNAPP) 24 March 1992 (24.03.92), claims (cited in the application). --	1,13, 14
A	EP, A1, 0 461 783 (KNAPP) 18 December 1991 (18.12.91), claims. ----	1,13, 14

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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
01 February 1994

Date of mailing of the international search report

Name and mailing address of the ISA
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

Authorized officer
SCHÄFER e.h.

Form PCT/ISA/210 (second sheet) (July 1992)

ANHANG ANNEX ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

au rapport de recherche international relatif á la demande de brevet international n°

PCT/US 93/10694 SAE 82385

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés á titre indicatif et n'engagent pas la responsibilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 5098819		US A 5278035	11-01-94
		AU A1 77187/91	23-01-92
		AU B2 622364	02-04-92
		CA AA 2042908	12-12-91
		EP A1 461783	18-12-91
		JP A2 4232944	21-08-92
EP A1 461783	18-12-91	US A 5278035	11-01-94
		AU A1 77187/91	23-01-92
		AU B2 622364	02-04-92
		CA AA 2042908	12-12-91
		JP A2 4232944	21-08-92