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— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF EXTRACTION OF EUROPIUM(III) AND/OR YTTRIUM(III) IONS FROM CONCENTRATE OF LUMINOPHORE DUST OR SLUDGE

(57) Abstract: The invention relates to a method of selective extraction of europium(III) and/or yttrium(III) ions from luminophore dust or sludge, the major components of which are oxides and sulphides of zinc, cadmium, yttrium and europium. From the concentrate of luminophore dust or sludge an aqueous solution is prepared and is subsequently contacted with an extraction agent, which is alkylphosphoric or dialkylphosphoric acid, either pure or diluted with an organic solvent. The reaction equilibrium is strongly dependent on the equilibrium concentration of free acid in the aqueous phase of the reaction. After separating the aqueous phase and the organic phase after the extraction, europium(III) and yttrium(III) ions are recovered from the organic phase.

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Method of extraction of europium(III) and/or yttrium(III) ions from concentrate of luminophore dust or sludge

Technical Field

The invention relates to selective isolation of yttrium and europium salts from the concentrate of luminophores, which was extracted by an inorganic acid, preferably hydrochloric acid or nitric acid. The concentrate of luminophores is obtained during the recycling of used screens of colour televisions or monitors.

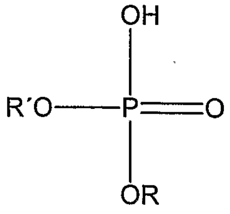
Background Art

The necessity of ecological reprocessing of the growing amount of electro technical wastes from households and the commercial sector leads to the introduction of new recycling technologies. With regard to the amount and harmfulness of the waste, one of the most important technologies is the reprocessing of used TV receivers and monitors of personal computers. In this process, major part of the waste as to the volume is glass. Especially barium and lead glass, used in the cathode-ray tube funnel and luminescent screens, is a valuable raw material. However, it must not be contaminated by the presence of luminiscent layer on the inner part of the screen. This luminophore, deposited in the form of powder layer, contains some elements, which change the optical properties of the glass and thereby make it less valuable for further use. The main source of this contamination are the compounds of yttrium and europium, the price of which is considerably high and therefore their isolation is economically desirable.

In order to maintain the value of the lead glass, the luminophore layer is mechanically, eventually also chemically removed (see the patent application PL 353981). The resulting dust, eventually sludge, containing luminescent substances, predominantly oxides and sulphides of zinc, cadmium, yttrium and europium, is so far deposited as toxic waste, because it contains heavy metals (zinc, cadmium). The present invention provides a method of isolation of valuable components (yttrium and particularly europium) present in the described concentrates, thereby significantly improving the economic balance of the recycling.

Disclosure of Invention

The object of the present invention is a method of extraction of europium(III) and/or yttrium(III) ions from the concentrate of luminophore dust or sludge, the major component of which are oxides and sulphides of zinc, cadmium, yttrium and europium. An aqueous solution is prepared from the concentrate of luminophore dust or sludge and said aqueous solution is subsequently contacted with an extraction agent of general formula I:



$$\mathrm{R'O{-}}\overset{\displaystyle \mathrm{OH}}{\underset{\displaystyle \mathrm{OR}}{\mathrm{P}}}\mathrm{{=}O}$$

I,

wherein R is linear or branched alkyl group containing 4 to 12 carbon atoms, and R′ is hydrogen atom or linear or branched alkyl group containing 4 to 12 carbon atoms;

whereas the extraction agent is either pure or diluted with an organic solvent. After separating the aqueous and the organic phase after the extraction, europium(III) and/or yttrium(III) ions are recovered from the organic phase.

The preparation of the aqueous solution from the concentrate of luminophore dust or sludge can be performed by e.g. dissolution in slight excess of inorganic acid. The term „inorganic acid“ means herein a common mineral acid, such as sulphuric acid, hydrochloric acid, nitric acid or perchloric acid. Preferably hydrochloric acid or nitric acid are used, because they both form soluble salts with the elements present in the luminophore. The use of sulphuric acid is less suitable, because yttrium(III) and europium(III) sulphides show a lower solubility in water. The use of other acids, such as perchloric acid, is possible, but uneconomical. The resulting extract is subsequently filtered. The overall concentration of metals in the extract should range from 0.01 mol/l to 1.5 mol/l. At a higher ionic strength of the solution, undesired solvation mechanisms of the extraction could take place.

The extraction agent of general formula I contains an acidic hydrogen atom, so that it can be generally abbreviated HL, wherein H is the cleavable acidic hydrogen atom and L is the organic residue of the molecule.

In the preferred embodiment, bis(2-ethylhexyl)phosphoric acid (HDEHP) can be used. The HDEHP is commonly used in hydrometallurgy for recovery and separation of some metals in solutions and can easily be used for the separation in the process of the invention. The reaction occurs in accordance with the below-indicated equation, wherein the symbol M denotes europium or yttrium, HL denotes monomeric molecule of HDEHP and the indexes aq., resp. org. denote aqueous, respective organic phase.

$$M^{3+}{}_{aq} + 3\ (\,HL\,)_{2\ org} \leftrightarrows M\,(\,HL_2\,)_{3\ org} + 3\ H^{+}{}_{aq}$$

The extraction agent can be diluted with various organic solvents, preferably aliphatic or aromatic hydrocarbons, optionally the mixtures thereof. Low solubility of the organic solvent in water, low volatility, low flammability and low toxicity are advantageous. Preferably octane, decane or xylene are used as organic solvents.

The extraction agent or its solution in the organic solvent reacts with the aqueous solutions of the yttrium(III) and europium(III) salts, prepared from the concentrate of luminophore dust or sludge, yielding organic complexes of these metals that migrate into the organic phase. The equilibrium of this reaction is strongly dependent on the equilibrium concentration of the free acid in the reacting aqueous phase. At a lower concentration of the free acid, the metal ions are extracted into the organic phase. Addition of inorganic acid into the aqueous phase causes the migration of the metal ions back to the aqueous phase. The ability of the metal ions to migrate into the organic phase or back to the aqueous phase is different for various elements present in the extract of luminophores, which allows the effective separation of the elements. The distribution of the metal(III) ion between the organic and the aqueous phase depends on the cube (third power) of the concentration of hydrogen ions in the aqueous phase and is therefore very steep (J. Phys. Chem. 1981, 85(24), pp. 3646-3651).

The equilibrium concentration of the free acid in the aqueous phase, suitable for the extraction of the yttrium(III) and europium(III) ions depends on the solvent used. Generally, in case of the europium(III) ion the distribution ratio between the organic and the aqueous phase equates one at the concentration of free acid in the aqueous phase ca 0.7 mol/l when using aliphatic solvents and ca 0.4 mol/l when using aromatic solvents. Also inside these general groups of solvents there are differences, depending on the length and structure of the chain. The suitable concentration of the free acid in the aqueous phase for the extraction of the europium(III) ions is in the range of from 0.1 to 1.5 mol/l. Yttrium(III) reaches the distribution ratio equal to one at the concentration of the free acid in the aqueous phase ca 1.8 mol/l. The suitable concentration of free acid in the aqueous phase for the extraction of yttrium(III) ions into the organic phase is 0.5 to 3.0 mol/l, for a fully selective extraction it ranges from 0.8 to 1.8 mol/l.

The major components of luminophore solutions are zinc, eventually cadmium, which have a low ability to extract in the extraction system of the present invention. A higher degree of extraction of these elements can be reached only at an the acidity of the aqueous phase lower than 0.1 - 0.2 mol/l, therefore these values of acidity should be avoided when removing impurities from yttrium and europium.

In the preferred embodiment, the yttrium(III) ions are selectively extracted from the aqueous extract of the concentrate of luminophore dust or sludge into the organic phase containing the extraction agent at the concentration of free acid in the aqueous phase from 0.8 to 1.8 mol/l and subsequently the europium(III) ions are extracted at the concentration of free acid in the aqueous phase from 0.2 to 0.7 mol/l. Other elements present in the concentrate of luminophore dust or sludge remain in the waste aqueous solution.

The europium (III) and yttrium (III) ions are then washed out from the organic extracts with 0.5 – 8 mol/l inorganic acid and can be subsequently chemically worked-up by processes commonly known in the art to yield a suitable product, such as yttrium (III) and europium (III) oxides.

In the countercurrent multi-stage embodiment of the extraction process it is possible to acquire almost any grade of purity of the individual components.

The present invention is further illustrated by the following examples, which should not be construed as further limiting.

Examples of carrying out the Invention

In the following examples the concentrations of metal ions were determined by atomic absorption spectroscopy (AAS), and the concentrations of free acid (H^+) were determined by titration with pH-electrode.

Example 1

1000 ml of 1 M solution of bis(2-ethylhexyl)phosphoric acid (HDEHP) in decane was shaken for 10 minutes with 1000 ml of the solution formed by dissolving 200 g of the luminophore concentrate in 25 % (w/w) HCl. The aqueous and the organic phase were separated. The initial composition of the aqueous solution and the resulting equilibrium concentrations of the components in the aqueous and the organic phase are listed in Table 1, which shows that the organic phase contains yttrium ions and only trace amounts of zinc and europium ions.

Table 1

ion	initial concentration in the aqueous solution [mol/l]	equilibrium concentration [mol/l]	
		aqueous phase	organic phase
Zn^{2+}	1,13	1,12	0,004
Y^{3+}	0,202	0,045	0,160
Eu^{3+}	0,042	0,040	0,002
H^+	1,81	2,27	-

Example 2

The resulting aqueous phase formed in Example 1 was partly neutralized by addition of 160 ml of 10 M ammonia solution and the volume was adjusted to 1000 ml. This initial solution was shaken with 1000 ml of 1 M solution of bis(2-ethylhexyl)phosphoric acid in decane (the same procedure as in Example 1). The resulting organic and aqueous phase were separated.

The initial composition of the aqueous solution and the resulting equilibrium concentrations of the components in the aqueous and the organic phase are listed in Table 2, which shows that the organic phase contains yttrium and europium ions.

Table 2

ion	initial concentration in the aqueous solution [mol/l]	equilibrium concentration [mol/l]	
		aqueous phase	organic phase
Zn^{2+}	1,02	1,00	0,03
Y^{3+}	0,038	0,001	0,036
Eu^{3+}	0,035	0,004	0,030
H^+	0,21	0,45	-

Example 3

1 M solution of the bis(2-ethylhexyl)phosphoric acid (HDEHP) in decane was contacted in a six-stage battery of mixers - separating vessels continually with the initial aqueous solution of the luminophore extract, the composition of which is shown in Table 3. The volume ratio of the organic phase to the aqueous phase was 3 : 1.

The resulting organic extract was subsequently washed in three stages, first with 0.8 M HCl solution (extract A) and then with 8 M HCl solution (extract B). The volume ratio of the organic phase to the aqueous phase was 3 : 1. The composition of the extracts is shown in Table 3: extract A contains europium ions and extract B yttrium ions.

In this process, the concentration of free acid in the aqueous phase of the extraction system in the course of the extraction reaction is ca 0.7 mol/l.

Table 3

ion	initial concentration in the aqueous solution [mol/l]	extract A [mol/l]	extract B [mol/l]
Zn^{2+}	1,01	0,001	0,001
Y^{3+}	0,176	0,002	0,170
Eu^{3+}	0,034	0,029	0,004
H^+	0,05	0,70	7,3

Example 4

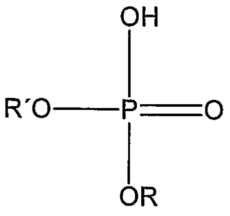
1000 ml of 1 M solution of bis(2-ethylhexyl)phosphoric acid (HDEHP) in xylene was shaken for 10 minutes with 1000 ml of the solution formed as in Example 1. The initial composition of the aqueous solution and the resulting equilibrium concentrations of the elements in the aqueous and the organic phase are shown in Table 4, which shows that the organic phase contains yttrium ions and only trace amounts of zinc ions.

Table 4

ion	initial concentration in the aqueous solution [mol/l]	equilibrium concentration [mol/l]	
		aqueous phase	organic phase
Zn^{2+}	1,13	1,13	0,001
Y^{3+}	0,202	0,166	0,035
Eu^{3+}	0,042	0,042	min.
H^+	1,81	1,90	-

CLAIMS

1. A method of extraction of europium(III) and/or yttrium(III) ions from the concentrate of luminophore dust or sludge, the major component of which are oxides and sulphides of zinc, cadmium, yttrium and europium, characterized in that an aqueous solution is prepared from the concentrate of luminophore dust or sludge and said aqueous solution is subsequently contacted with an extraction agent of general formula I,



$$R'O-P(=O)(OH)-OR$$

I

wherein R is linear or branched alkyl group containing 4 to 12 carbon atoms,

and R′ is hydrogen atom or linear or branched alkyl group containing 4 to 12 carbon atoms;

whereas the extraction agent is pure or diluted with an organic solvent;

and after separating the aqueous and the organic phase after the extraction, europium(III) and/or yttrium(III) ions are recovered from the organic phase.

2. The method of extraction of europium(III) and/or yttrium(III) ions according to claim 1, characterized in that the extraction agent is bis(2-ethylhexyl)phosphoric acid.

3. The method of extraction of europium(III) and/or yttrium(III) ions according to claim 1 or claim 2, characterized in that the organic solvent, in which the extraction agent is dissolved, is aliphatic or aromatic hydrocarbon or their mixture.

4. The method of extraction of europium(III) and/or yttrium(III) ions according to claim 1 or claim 2, characterized in that the organic solvent in which the extraction agent is dissolved, is octane, decane or xylene.

5. The method of extraction of europium(III) ions according to any of claims 1 to 4, characterized in that the equilibrium concentration of free acid in the aqueous phase of the extraction system is 0.1 to1.5 mol/l.

6. The method of extraction of yttrium(III) ions according to any of claims 1 to 4, characterized in that the equilibrium concentration of free acid in the aqueous phase of the extraction system is 0.5 to 3.0 mol/l.

7. The method of extraction of yttrium(III) ions according to any of claims 1 to 4, characterized in that the equilibrium concentration of free acid in the aqueous phase of the extraction system is 0.8 to 1.8 mol/l.

8. The method of extraction of yttrium(III) ions and subsequent extraction of europium(III) ions according to any of claims 1 to 4, characterized in that at first yttrium(III) ions are extracted at the equilibrium concentration of free acid in the aqueous phase of the extraction system ranging from 0.8 to 1.8 mol/l and subsequently europium(III) ions are extracted at the equilibrium concentration of free acid in the aqueous phase of the extraction system ranging from 0.2 to 0.7 mol/l.

9. The method of extraction of europium(III) and/or yttrium(III) ions according to any of the preceding claims, characterized in that it is performed in the countercurrent multi-stage embodiment of the extraction process.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2005/000088

A. CLASSIFICATION OF SUBJECT MATTER
C22B3/38 C22B7/00 C22B59/00 C22B3/10

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)
C22B

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, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	US 3 110 556 A (PEPPARD DONALD F ET AL) 12 November 1963 (1963-11-12) column 5, line 34 - line 45; claims 1,2,5,11-14; figures 1-3	1-7,9 8
Y	US 3 524 723 A (WAYNE A. MILLSAP ET AL) 18 August 1970 (1970-08-18) column 2, line 6 - column 3, line 44; claims 1,2; examples 1-3	1-7,9
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2005/000088

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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A	column 4; figure 1 -----	5-8

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Information on patent family members

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