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[54] RECOVERY OF ZINC AND NICKEL FROM WASTE PHOSPHATE LIQUOR

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[73] Assignee: **The United States of America as represented the Secretary of the Interior**

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[51] **Int. Cl.** **B01d 11/04,** C01g 9/00, C01g 53/00

[58] **Field of Search** .....23/312 R, 312 P, 312 ME, 309, 23/165; 210/21, 38, 40

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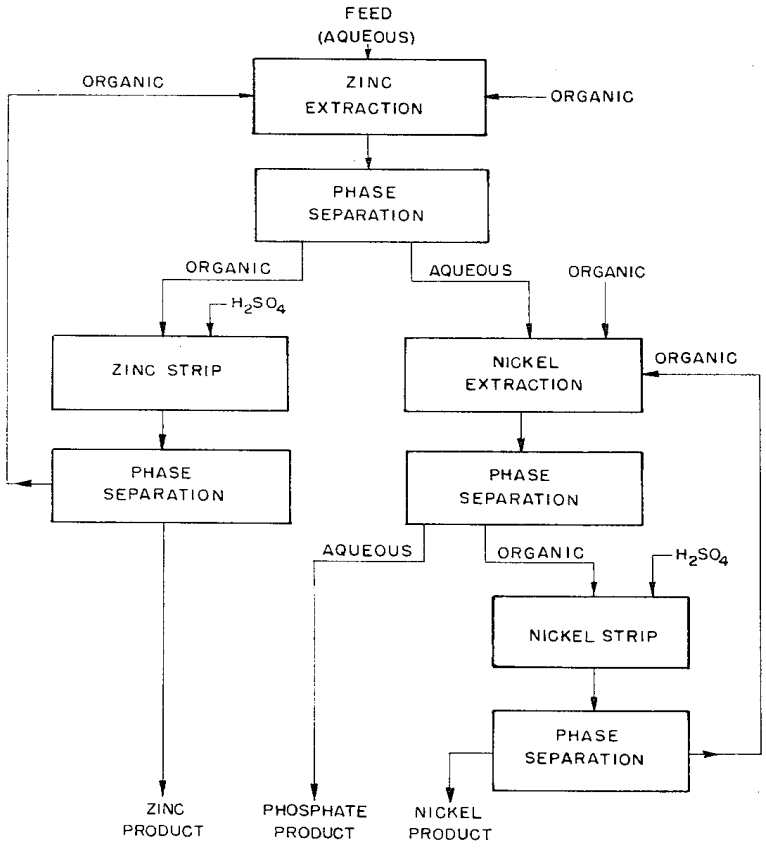
[57] **ABSTRACT**

Zinc and nickel are recovered from waste phosphate liquor by solvent extraction. Zinc is first extracted with di-2-ethylhexyl phosphoric acid in an organic diluent. Nickel is then extracted from the raffinate of the zinc extraction with dinonyl naphthalene sulfonic acid in an organic diluent.

4 Claims, 1 Drawing Figure



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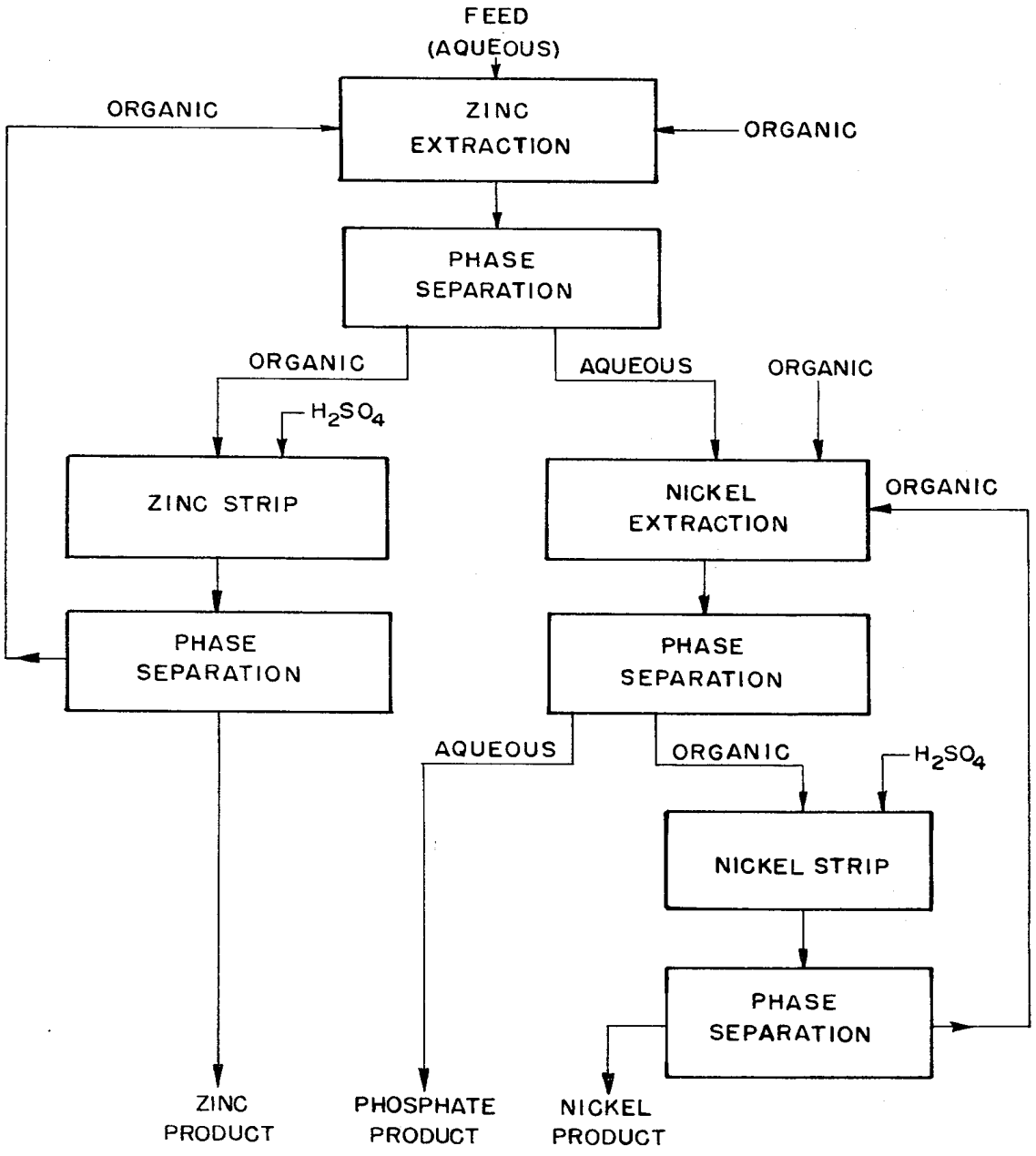

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RECOVERY OF ZINC AND NICKEL FROM WASTE PHOSPHATE LIQUOR

Phosphate coating of metals is widely used in industry, especially in the manufacture of steel products, for several purposes: to provide a base to which paint or enamel will strongly adhere, for corrosion protection, for lubrication in die-forming operations, and to provide a porous surface that will absorb and retain lubricating oil. The phosphating solution consists essentially of phosphoric acid, a primary phosphate of iron, zinc, or manganese, and oxidizing agents such as nitrites, nitrates, chlorates, and peroxides. The phosphate coating reaction is based on the insolubility in water and solubility in acids of most metal phosphates. When steel is contacted with the phosphating solution, iron is dissolved, hydrogen is evolved, and the primary metal phosphates are converted to insoluble secondary and tertiary phosphates that deposit on and strongly bond to the metal surface.

The wastes from such phosphating operations, which consist of spent phosphating solution and an insoluble sludge, are often discharged to streams or ground waters. This contributes to stream pollution problems, and also represents large losses of nickel and zinc, as well as phosphates and lesser amounts of copper, manganese and lead. Recovery of nickel and zinc in useful form from such wastes is not undertaken to any extent by the metal processing industry.

It has now been found, according to the process of the invention, that nickel and zinc may be selectively recovered from waste phosphate liquors by means of a specific solvent extraction procedure. This procedure involves initial extraction of zinc with di-2-ethylhexyl phosphoric acid (EHPA) in an organic diluent, e.g., kerosene, followed by extraction of nickel from the raffinate of the zinc extraction with dinonyl naphthalene sulfonic acid (DNSA) in an organic diluent.

The drawing is a flowsheet of the process of the invention.

EHPA exists as a dimer, $(RH)_2$, in kerosene and the generalized equation for the Zn extraction reaction is believed to be:

$$Zn_{aq}^{+2}+2(RH)_{2\ org} \rightarrow Zn(R_4H_2)_{org}+2H^+_{aq}$$

DNSA is believed to exist as a polymer, $(RH)_x$, in solution and the equation for the Ni extraction is believed to be:

$$Ni^{+2}_{aq}+(RH)_{x\ org} \rightarrow Ni_{x-2}R_{x\ org}+2H^+_{aq}$$

Compositions of the waste phosphate liquors may vary considerably depending on the process from which they are derived. Generally, however, they will consist of aqueous solutions containing about 0.5 to 2.5 grams per liter of Ni, 0.5 to 3.5 grams per liter of Zn, 3.0 to 6.0 grams per liter of phosphate as PO_4 with smaller amounts of Cu, Mn, and Pb. The pH of the solution will usually range from about 3.0 to 3.5. pH values substantially below or above these values may result in inefficient extraction or undesired precipitation. Use of pH values of about 3.0 to 4.0 usually result in more efficient extraction of Zn, while pH values of about 2.0 to 3.0 are more efficient for Ni extraction. Any mineral acid, alkali metal hydroxide, or ammonium hydroxide may be used for initial adjustment of pH, if required; however, phosphoric acid or sodium hydroxide is preferred.

Kerosene is the preferred diluent for extraction of Zn. However, other conventional organic diluents, or carriers, such as fuel oil, gasoline, or other petroleum products, may also be used. Optimum concentrations of EHPA vary in the diluent may vary considerably, depending on the composition of the waste phosphate liquor, type of diluent used, etc. However, concentrations of from about 5 to 30 volume percent are usually satisfactory. The optimum amount of extractant, i.e., EHPA-diluent solution, used will also very widely depending on the nature of the waste phosphate liquor and diluent, type of extraction process, desired degree of removal of Zn, etc. A volume ratio of extractant-to-waste phosphate liquor of about 2:1 to 1:2 is, however, usually satisfactory.

The preferred diluent for Ni extraction is butyl ether, provided the Zn has been substantially completely removed prior to extraction of Ni. Otherwise, another of the diluents disclosed above may be preferred, since butyl ether exhibits a considerable affinity for Zn. Concentrations of DNSA in the diluent will usually range from about 5 to 20 volume percent, with the volume ratio of extractant-to-waste phosphate liquor (raffinate from Zn extraction) being in the range of about 2:1 to 1:2.

The process of the invention may be utilized as a batch or as a continuous process. It may be carried out as a batch process in an open container equipped with suitable stirring device and drain opening to permit separation of the phases, such container serving both as mixer and settler cell. The organic phase may be retained in the cell and stripped as in the extraction cycle. As a continuous process, commercially available countercurrent equipment including box type, cascade type, or reciprocating plate are all effective.

Extraction of both Zn and Ni are carried out at room temperature and pressure. A contact time of as little as 1 or 2 minutes for Ni extraction and about 5 minutes for Zn extraction is usually sufficient. However, longer periods, e.g., about 20 minutes or more may be necessary for maximum extraction in some cases. Where a batch extraction process is employed, several extraction stages may be required if maximum extraction is desired. Generally, three to five stages will extract either Zn or Ni almost completely.

Following extraction, both Zn and Ni are recovered from the organic extractant by stripping with an aqueous acid solution. The preferred stripping solution is a dilute, i.e., 15 volume-percent, solution of sulfuric acid. However, other acids such as hydrochloric may be used for stripping. This treatment also regenerates the EHPA and DNSA, which may then be recycled for reuse in the extraction process.

The raffinate, following extraction of both Zn and Ni, consists largely of an aqueous solution of phosphoric acid, sodium phosphate and sodium nitrate. This solution may be reacted with ammonia, ammonium hydroxide or potassium hydroxide to form a mixed fertilizer material.

The invention will be more specifically illustrated by the following example.

EXAMPLE

A waste phosphate solution from automobile assembly plants containing 1.34 gpl Zn, 1.10 gpl Ni, and 3.8 gpl PO_4 was adjusted to a pH value of 4.5 by addition of sodium hydroxide. One hundred ml. of this solution and 100 ml. of extractant comprising 20 volume percent EHPA in kerosene were thoroughly mixed in a 500 ml. separatory funnel by mechanical shaking for a period of 20 minutes. The organic and aqueous phases were then separated. No adjustment of pH of the aqueous phase was necessary as the extraction of zinc lowered to the pH to 2.4.

One hundred ml. of extractant comprising 8 volume percent of DNSA in a 4 to 6 mixture of butyl ether and heptane were mixed with the raffinate from the Zn extraction by the same procedure as above. Again, the organic and aqueous phases were separated.

The organic phases from the preceding steps were then separately stripped with 100 ml. of 15 percent sulfuric acid by mechanical soaking for 20 minutes in a 500 ml. separatory funnel. The phases were then separated and the aqueous phase analyzed for Zn and Ni, respectively. Results showed that 99.5 percent of the Zn and 98.5 percent of the Ni were extracted.

Repeated extractions according to the above procedures showed that three and five stages of extraction was sufficient to substantially completely extract the Zn and Ni, respectively.

What is claimed is:

1. A method for recovery of zinc and nickel from waste phosphate liquor, said liquor consisting essentially of an aqueous solution containing 0.5 to 2.5 grams per liter of nickel, 0.5 to 3.5 grams per liter of zinc and 3 to 6 grams per liter of phosphate, comprising (1) adjusting the pH of the liquor to about 3 to 4 and extracting zinc with an extractant comprising about 5 to 30 volume percent of di-2-ethylhexyl phosphoric acid in an organic diluent and (2) adjusting the pH of the raf-

finate from the zinc extraction to about 2 to 3 and extracting nickel with an extractant comprising about 5 to 20 volume percent of dinonyl naphthalene sulfonic acid in an organic diluent.

2. The method of claim 1 in which the organic diluent in the zinc extractant is kerosene.

3. The method of claim 1 in which the organic diluent in the nickel extraction is butyl ether.

4. The method of claim 1 in which both the zinc and the nickel are recovered from the organic extractant by stripping with a sulfuric acid solution.

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