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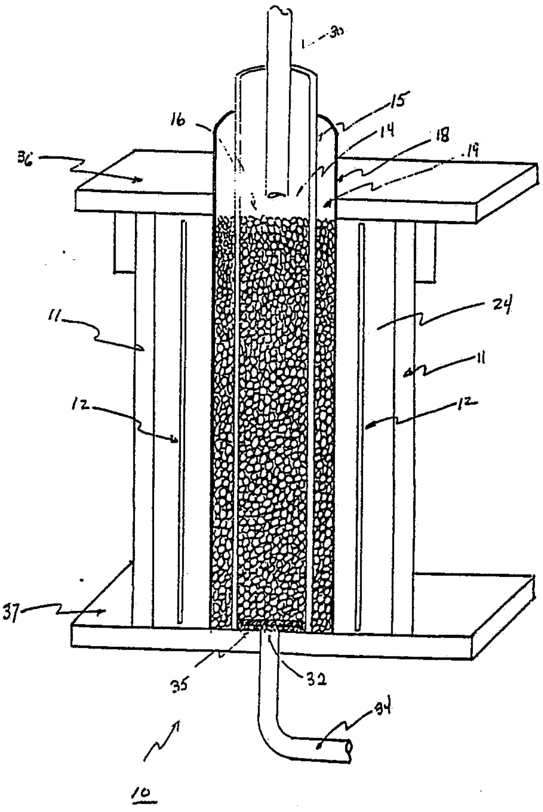
**(54) Title:** PROCESS OF RECLAIMING BATTERY ACID FROM LEAD ACID BATTERIES

**(57) Abstract**

The present invention discloses a process of extraction and filtration for removing iron impurities from the acid in used lead-acid batteries. Produced is a reclaimed battery acid which performs very well in new batteries and avoids costs and environmental risks entailed with present methods. In the preferred embodiment, the present invention discloses a process for rejuvenation of strip acid employed in such reclamation. In the process of removing impurities from battery acid through extraction, the extractant becomes loaded with impurities and loses its effectiveness. Extractant may be regenerated by contacting it with a strip acid. A reduction process is employed to regenerate the strip acid so that it may be used repeatedly. By recycling the extractant and the strip acid in the present invention, the present process further increases the effectiveness of battery acid regeneration--producing a reclaimed battery acid fluid which performs very well in new batteries and substantially reducing by-product waste in the regeneration of the battery acid.



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# Process of Reclaiming Battery Acid from Lead Acid Batteries

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to an improvement in the method of removing contaminating impurities from used battery acid fluid through extraction and filtration so to permit the fluid to be used in new batteries or concentrated for sale. In particular, the method employs a solvent extractant to remove contaminating iron impurities from battery acid and a reduction process to regenerate strip acid employed in rejuvenating iron removing extractant.

### 2. Description of the Prior Art

A serious problem, both economically and environmentally, in the manufacture and sale of lead-acid batteries is how to handle and dispose of contaminated battery acid fluid contained in discarded batteries. Until relative recent environmental regulations ended the practice, this waste, comprising sulfuric acid ($H_2SO_4$) diluted with various metal and non-metal contaminents, traditionally has been dumped in landfills or flushed into public sewers. The advent of severe pollution penalties has ended this practice, but, until now, no reasonable alternative plan of disposal has been developed.

Presently, battery acid fluid from trade-in batteries is handled in a number of less than ideal manners. Some manufacturers have found an outlet through industries with demand for dilute sulfuric acid. However, this places the battery manufacturers at the mercy of the demands of other markets, and presents a whole host of problems when faced with the advent of cradle-to-grave environmental laws. Other manufacturers have paid to have the battery acid fluid neutralized and then disposed of in certain restricted landfills. This can be very expensive and is needlessly wasteful.

In the course of developing the present invention, the inventors encountered a number of proposals for reclamation of battery acid fluid. One solution proposed was distilling the sulfuric acid via indirect heat in closed vessels under vacuum. This was dismissed as unreasonable in light of high energy costs, high investment costs, serious corrosion and disposal problems, and environmental concerns. Another solution proposed was acid retardation in the form of an ion exchange process entailing passing a strong acid feed through a strong base ion exchange resin. Once again this proposal proved unreasonably expensive in investment and development costs. A further proposal was to remove contaminents through electrolytic processing. Despite early promising results using this method, further tests demonstrated that iron removal was insufficient for commercial purposes.

In light of the foregoing, it is a primary object of the present invention to avoid the waste and expense of disposal of contaminated battery acid fluid by providing a method of reclaiming contaminated battery acid fluid for use in new batteries or for concentration for resale.

It is an additional object of the present invention to increase the efficiency of the basic battery acid reclamation process by maximizing the amount of iron which can be removed from extractant through strip acid treatment.

It is a further object of the present invention to provide an entire method of battery acid fluid reclamation which is commercially practical, requires minimal capital investment, is relatively inexpensive to operate, and minimizes environmental risk.

## SUMMARY OF THE INVENTION

The present invention employs extraction and filtration steps to remove disabling iron impurities from used lead-acid battery acid fluid. Use of the present invention eliminates a serious environmental disposal problem, and produces a reclaimed battery acid fluid which performs as well as fresh battery acid fluid.

The present invention employs an extraction agent comprising a mixture of a chelating agent, such as a derivative of a 8-hydroxyquinoline, an organophosphoric acid, a modifier, and a hydrocarbon carrier solution. Using multiple extraction steps, the extraction agent is mixed with contaminated battery acid fluid (diluted with distilled water or dilute sulfuric acid water) to remove the metallic impurities. The extracted battery acid fluid is then filtered through a carbon filter to remove residual organics. The metallic impurities are subsequently removed from the extraction agent in a concentrated form.

Through concentration or the addition of fresh sulfuric acid to overcome the water dilution, the reclaimed battery acid fluid may be placed in new lead-acid batteries. Tests reveal that this process produces a battery acid fluid which performs as well as fresh battery acid fluid, but is free of the costs and environmental risks of disposing of used battery acid fluid.

The preferred embodiment of the present invention employs electrolytic treatment of strip acid to improve further the efficiency of, and further reduce the waste from, the process of removing iron impurities from lead-acid battery electrolyte solution through steps of extraction and filtration. This greatly reduces by-product waste in the sulfuric acid reclamation process while continuing to produce a reclaimed battery acid fluid which performs as well as fresh battery acid fluid.

The largest by-product of the basic reclamation process disclosed herein is the strip acid which is employed to rejuvenate the iron extractant. By increasing the amount of iron the strip acid can hold while still being able to rejuvenate the extractant, the efficiency of the entire system is greatly increased while the amount of waste generated by the system is greatly decreased. The preferred embodiment of the present invention discloses a process which substantially increases the effective iron holding capacity of the strip acid.

The affinity for iron of the extractant employed in the basic process is limited to ferric ($Fe^{+3}$) ions. It has been determined that by treating the strip acid to reduce the iron contained in it from ferric to ferrous ($Fe^{+2}$) form, the strip acid may then be further contacted with extractant with essentially no decrease in the stripping efficiency of the strip acid. In this manner the strip acid may be used repeatedly, with a vastly increased total iron content, before the strip acid must be replaced.

The present invention increases the overall efficiency of the reclamation process and decreases the by-product waste generated by the process while adding little cost to the process and no decrease in the effectiveness of the battery acid produced.

## DESCRIPTION OF THE DRAWING

Figure 1 is a cross-sectional view of the strip acid iron reduction cell of preferred embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an improved method of processing contaminated battery acid fluid into reclaimed battery acid fluid through use of liquid-liquid extraction and filtration.

Battery acid fluid removed from used lead-acid type batteries can be reclaimed through a series of dilution, filtration, extraction, and concentration steps. The process entails treating battery acid fluid removed from used lead-acid type batteries comprising approximately 25% (1.18 specific gravity) sulfuric acid ($H_2SO_4$) diluted with various metallic impurities, including iron (about 40-150 ppm), and reducing the contaminating iron level to an acceptable level of less than 20 ppm. The process is set forth below.

First, the contaminated battery acid fluid is filtered through a conventional filter to remove suspended particle matter. Commercially available hydrolytic polypropylene filters have proven effective for this purpose.

Next, the battery acid is diluted using distilled water or dilute sulfuric acid water to a level of 15 to 18% sulfuric acid. This is in accordance with the work by Demopoulous and Gefvert reported in "Iron(III) Removal from Base-Metal Electrolyte Solutions By Solvent Extraction," 12 Hydrometallurgy 299, 303 (1984), which teaches that iron removal via extraction from an electrolytic solution is maximized in the area of 150 to 180 grams per liter (g/l) of $H_2SO_4$.

Although battery acid fluid normally contains iron in its ferric (Fe III) form, it has been found that satisfactory extraction using the below identified extraction agent will not occur if the iron is in a ferrous (Fe II) form. Accordingly, if a substantial quantity of ferrous iron is present, the fluid should be oxidized using conventional methods, such as blowing it with air or adding peroxide, to form ferric iron prior to extraction.

Liquid-liquid extraction is then performed on the contaminated battery acid fluid. The extraction agent employed is a mixture of a chelating agent, an organophosphoric acid, and a modifier, all dissolved in a water immiscible carrier. Use of such a compound for extraction of high concentrations of metals from electrolyte solution is disclosed in United States Patent 4,067,802.

Specifically, the chelating agent employed is an 8-hydroxyquinoline substituted in the No. 7 position with a long chain aliphatic hydrocarbon radical ("8-hydroxyquinoline derivative"), and particularly a 7-[3-(5,5,7,7-tetramethyl-1-octenyl)] -8-hydroxyquinoline. This is commercially available under the trademark KELEX 100 produced by SHEREX Chemical Co., Inc. The organophosphoric acid is preferably a mono- or dialkyl phosphoric acid, such as a di-2-ethylhexyl phosphoric acid ("DEHPA"). The respective 8-hydroxyquinoline derivative and the organophosphoric acid are mixed at a molar ratio between 1:1 to 1:4. The modifier serves to maintain the solubility of the extraction agent in the carrier and enhances the phase disengagement. It may be either alkyl phosphates or high molecular weight alcohols. Tridecanol is preferred.

As is disclosed in United States Patent 4,067,802, the water immiscible carrier should be a hydrocarbon solvent which dissolves both the chelating agent and the phosphoric acid and should be chemically stable, low in toxicity, and have a high flash point. Preferred is odorless mineral spirits.

A mixture containing 30% extraction agent and 70% mineral spirits typically comprises 6.8 volume % (within a range of 5 to 10%) of 8-hydroxyquinoline derivative, 12.4 volume % (within a range of 10 to 15%) DEHPA, and 10.8 volume % (within a range of 5 to 10%) tridecanol. The ratio of extraction agent to mineral spirits may range from 5:95 to 50:50.

The extraction mixture is then mixed with the diluted contaminated battery acid fluid in ratios ranging from 4:1 to 1:4. The preferred mixture is at a ratio of about 1:1 with the use of multiple extraction steps, where necessary.

Once the iron content is brought to levels of 20 ppm, the extracted battery acid fluid is then passed through a polish filter which comprises a granular or powdered activated carbon filter, such as a packed column or flat bed filter unit. Activated carbon sold under the trademark NUCHAR SA by Westvaco has proven effective in removing both organics and some metallic impurities. This removes unwanted organic impurities from the solution, such as residual extraction agent, and produces the reclaimed battery acid fluid. When the flow from the carbon filter is no longer clear, the carbon is replaced.

Finally, the 15% acid may be concentrated under vacuum by heating, or concentrated sulfuric acid may be added to the reclaimed battery acid fluid, to return the fluid to approximately 35% sulfuric acid (1.265 specific gravity). The reclaimed battery acid fluid may then be placed in new batteries.

As the following examples of this basic process demonstrate, the present invention performs exceptionally well.

EXAMPLE 1: A contaminated battery acid fluid was tested consisting of:

| Component | Amount |
|---|---|
| $H_2SO_4$ | 25% |
| Fe | 185 ppm |
| Sb | 20 ppm |
| Pb | <2 ppm |
| As | 3 ppm |
| Cu | 10 ppm |
| Ni | <2 ppm |
| Cd | 20 ppm |

The contaminated battery acid fluid was diluted using distilled water to a level of 15% $H_2SO_4$. It was then extracted using an extraction agent of 6.8% KELEX 100, 12.4% DEHPA, 10.8% tridecanol, and 70% odorless mineral spirits. The mixture was at a volumetric ratio of 1:1 battery acid fluid to extraction mixture. Three separate extractions were performed.

The extracted battery acid fluid was then passed through a packed bed of activated carbon (NUCHAR SA). Finally, sulfuric acid was added to bring the fluid back to the desired acid concentration. The resulting reclaimed battery acid fluid consisted of:

| Component | Amount |
|---|---|
| $H_2SO_4$ | 30 % |
| Fe | 20 ppm |
| Sb | 6 ppm |
| Pb | <2 ppm |
| As | 3 ppm |

| | |
|---|---|
| Cu | 6 ppm |
| Ni | <2 ppm |
| Cd | 9 ppm |

This fluid was tested against control batteries containing fresh sulfuric acid, a solution of fresh sulfuric acid solution diluted with contaminated battery acid, and a solution of contaminated battery acid fluid passed through a NUCHAR SA carbon filter.

The results revealed that the present invention produced a battery acid fluid which performed as well as the fresh fluid in every respect, including cold cranking power, reserve capacity, charge rate acceptance, shelf life, "gassing," and performance drop. In each case, the other batteries performed significantly less effectively and had a current acceptance much less than the battery produced using the present invention.

EXAMPLE 2: A contaminated battery acid fluid was tested consisting of:

| Component | Amount |
|---|---|
| $H_2SO_4$ | 25 % |
| Fe | 63 ppm |
| Sb | 30 ppm |
| Pb | 3 ppm |
| As | 4 ppm |
| Cu | 16 ppm |
| Ni | 2 ppm |
| Cd | 12 ppm |

The contaminated battery acid fluid was diluted using distilled water to a level of 15% $H_2SO_4$. It was then extracted using an extraction agent of 6.8% KELEX 100, 12.4% DEPHA, 10.8% tridecanol, and 70% odorless mineral spirits. The mixture was at a volumetric ratio of 1:1 battery acid fluid to extraction mixture. Five separate extractions were performed.

The extracted battery acid fluid was then passed through a packed bed of activated carbon (NUCHAR SA). Finally, sulfuric acid was added to bring the fluid back to the desired acid concentration. The resulting reclaimed battery acid fluid consisted of:

| Component | Amount |
|---|---|
| $H_2SO_4$ | 30% |

| | |
|---|---|
| Fe | 6 ppm |
| Sb | 6 ppm |
| Pb | <2 ppm |
| As | 1 ppm |
| Cu | 3 ppm |
| Ni | <2 ppm |
| Cd | 4 ppm |

Tests revealed that this sample performed at least as well as the fluid produced in Example 1.

EXAMPLE 3: A further test was conducted employing a ratio of 20% extraction agent and 80% mineral spirits. This mixture proved to perform nearly as well as a mixture of 30% extraction agent and 70% mineral spirits. A mixture of 10% extraction agent and 90% mineral spirits proved to be ineffective.

It has been found that the above extraction agent may be reclaimed and further, used indefinitely. This is accomplished by contacting the extraction agent with a strip acid which removes the contaminating iron content. The process disclosed entails repeatedly mixing the extraction agent with a strip acid of approximately 35% $H_2SO_4$ (within a range of 30 to 50% $H_2SO_4$), the metal contaminants will pass from the extraction agent to the strip acid. Waste is further lessened by repeatedly using the strip acid. Using either conventional cross flow or conventional counter current flow techniques, the strip acid may be used for multiple extraction steps: the purest strip acid is used to remove contaminants from the purest extraction agent, and then it is reused to remove contaminants from less pure extraction agent; this process continues until the strip acid is effectively loaded with contaminants.

A separate stripping test was performed to determine the efficiency of the strip acid process. In this test, the same quantity of acid was used repeatedly to regenerate previously used extractant. It was found that levels of iron in excess of 1000 ppm did not reduce the stripping efficiency as long as the acid strength of the strip acid was maintained at 35% by the addition of concentrated acid, or within a concentration range of approximately 400 g/l to 500 g/l. This is due to the fact that the extractant transfers acid from a more concentrated stream (the strip acid) to a less concentrated stream (the battery fluid). The overall effect is that the iron in the strip acid is concentrated by a factor of 5-30 times as compared to waste battery fluid. As is explained, under these conditions, a two-stage cross flow technique is believed to function quite well to regenerate the extraction agent -- fresh acid used to strip partially clean extraction agent in stage-two, and contaminated acid (e.g. strip acid too contaminated to continue to serve in stage-two) employed in stage-one to produce partially clean extraction agent for stage-two. Once the strip acid lost its ability to strip iron from extractant, it was believed that the only option was to dispose of it through conventional disposal techniques.

The preferred embodiment is based on further work directed at improvement in the efficiency of this extractant reclamation process. It has been determined that the efficiency of the entire strip acid regeneration process may be improved significantly through use of carbon or electrolytic treatment of the strip acid. As has been discussed above, it is known that the extractant absorbs iron only when it is in a ferric (Fe III) state; the extractant is essentially "blind" to iron in the ferrous (Fe II) state. By treating the used strip acid to reduce the iron ions from ferric to ferrous, it has been determined that the strip acid may be re-used to regenerate extractant with no adverse effect on the regeneration process-- the extractant continues to release its ferric iron content to the strip acid while re-absorbing none of the ferrous iron contained in the strip acid. In this manner, the strip acid can be used and re-used far beyond the level of iron stripping effectiveness previously achieved.

The effectiveness of the strip acid reclamation process of the present invention is demonstrated by the following examples:

EXAMPLE 4:

As a control, battery acid regeneration and extractant reclamation was performed in a continuous pilot plant in the manner disclosed above. This process comprised treating contaminated sulfuric acid from lead-acid batteries in a six stage counter-current extraction circuit with an extraction agent containing 6.8 v/o Kelex 100, 12.4 v/o DEHPA, 10.8 v/o tridecyl alcohol, and 70 v/o odorless mineral spirits (30%

Sherex Iron Reagent / 70% mineral spirits). The extraction agent, loaded with 30-40 ppm ferric iron, was regenerated (i.e. "stripped") with 35% sulfuric acid to remove the iron. The strip acid was reused until it was no longer able to remove iron from the extraction agent. The iron level in the strip acid reached a maximum of about 450 ppm.

EXAMPLE 5:

Loaded extraction agent, generated as in Example 4, was stripped with 35% sulfuric acid. The strip acid was passed from a strip acid reservoir through a bed of activated carbon prior to reusing it in order to reduce the contained iron from ferric to ferrous. The carbon in the bed was replaced when no increase in the iron concentration of the strip acid was measured. The maximum level of iron in the strip acid reached about 1120 ppm.

EXAMPLE 6:

The activated carbon bed used in Example 5 was removed from the circuit. Two electrodes (an anode and a cathode), connected to a D.C. power source, were placed in the strip acid reservoir. The anode was placed inside an envelope made of a microporous polyethylene diaphragm material (specifically, material supplied by W.R.Grace & Co. under the trademark DARAMAC) to separate it from the strip acid in the reservoir. The envelope was filled with 35% sulfuric acid. An electric current of 1 amp at 3 volts was passed through the cell, causing oxygen gas to be liberated at the anode and iron to be reduced from ferric to ferrous at the cathode (as well as having hydrogen gas liberated at the cathode). Using this method, the iron level in the strip acid reach a level of 2600 ppm before losing effectiveness and the ferric ion content of the strip acid was maintained below 500 ppm.

It is preferred that the invention be carried out in a flow-through cell which permits the continuous treatment of strip acid. One such cell is shown in Figure 1. The cylindrical cell 10 includes an outer wall 11, an anode 12, a separator 18 and a cathode 14. The anode 12 and the cathode 14 are connected to a d.c. power supply (not shown). The cathode 14 comprises a current carrier such as a lead grid 15 and pieces of either activated carbon, coke or graphite 16. It has been determined that other material may be substituted for the packed bed just as effectively so long as it is not attacked by the acid; this may include crushed battery casings. The anode 12 comprises lead grid also. It should be understood that, without departing from the intent of the present invention, the anode 12 and the cathode 14 may be constructed from any suitable electrode material, including lead, carbon or titanium.

The cylindrical cathode 14 is housed within a separator wall 18 which defines the cathode chamber 19. The separator wall 18 shown is a cylinder constructed from a battery separator-type material. In the preferred embodiment, the separator material is an ion exchange membrane, such as the material sold under the trademark "IONAC MA 3475 Anion Membrane" by Sybron Chemicals, Inc., Birmingham, NJ. Other battery separator-type materials which will prevent mixing of the acid solutions in the cathode chamber and the anode chamber may be employed, including microporous polyethylene film, asbestos cloth or glass frit.

The anode chamber 24, which houses the cylindrical anode 12, surrounds the cathode chamber 19 and is enclosed in a length of PVC pipe 11 which is wider and concentric with the cathode chamber 19. Although PVC pipe and plate has been used in this embodiment for the wall 11 and for the top 36 and the bottom 37, it should be understood that any other material resistant to sulfuric acid and electrolytic processes may be substituted for one or all of these elements, including glass, polypropylene or teflon.

The electrical requirements of the cell 10 of the present invention are dependent upon a number of factors, including the size of the electrodes, the spacing of the electrode (i.e. the larger the cell 10, the greater the required voltage), and the size of the cell 10. The voltage through the cell 10 must be great enough to overcome the hydrogen potential on the cathode 14, the oxygen potential on the anode 12 and the resistance of the acid solutions. The ideal current density on the electrodes 14, 12 should be maintained within the range of 5 amps per sq. ft. to 25 amps per sq. ft. It is believed that the minimum voltage across the cell 10 should be about 3 volts. Additionally, it is believed that the cathode compartment 19 should be designed to be the minimum operative volume so to prevent backmixing of the treated and untreated strip acid.

In operation, the anode chamber 24 is filled with acid of the same concentration as the strip acid to the desired level. Used strip acid to be treated is introduced into the cell 10 from one or more intake lines 30 in the top of the cell 10. An outlet drain 32, covered with a polypropylene screen 35, is provided in the base of the cathode chamber 19 to carry away treated (reduced) strip acid. The level of strip acid in the cell 10 may be readily controlled by attaching a drain pipe 34 to the drain hole 32 and raising or lowering the pipe to achieve the desired fluid level within the cell 10. By applying an electric current through the cell 10 within the range of 0.5 amps at 3 volts to 3 amps at 4 volts, with the ideal range believed to be 1 amp at 3 volts to 2 amps at 3.3 volts, the strip acid can be continuously reduced and reused. The construction of the cell 10 allows it to be readily attached in-line in a continuous battery acid reclamation process. Under these electrical conditions, a cell 10 with an internal total volume of 0.6 liters should be able to treat continuously 0.6 to 3.0 liters per hour. It should be understood that the design of the electrolytic cell may be any desired shape, including cylindrical or rectangular (flat plate electrodes), without departing from the intent of the present invention.

The effective operation of the present invention should be appreciated by the following example:

EXAMPLE 7:

A flow-through cell, as above described, was employed with an applied current of 2 amps at 3.3 volts. Using the above described method, the iron level in the first stage strip acid reached a level of 4135 ppm without losing effectiveness and the ferric ion content of the strip acid was maintained below 100 ppm.

The above examples reveal that the present invention further eliminates the waste problem of disposing of contaminated battery acid fluid by dramatically increasing the usefulness and effectiveness of the strip acid extraction agent reclamation process disclosed in the parent application.

While particular embodiments of the present invention have been disclosed herein, it is not intended to limit the invention to such a disclosure, and changes and modifications may be incorporated and embodied within the scope of the following claims.

What is claimed is:

1. A method for recycling contaminated sulfuric acid from lead acid batteries to reclaimed sulfuric acid for reuse in said batteries by removing contaminating iron impurities, the steps which comprise:

(a) diluting the contaminated sulfuric acid to a concentration between 150 and 230 grams per liter;

(b) filtering the sulfuric acid through a first filter means to remove solid impurities;

(c) adding an oxidizing agent to the sulfuric acid to assure that the iron contaminants are substantially in a ferric form;

(d) removing the iron contaminants from the sulfuric acid through liquid-liquid extraction using an extraction agent comprising a mixture of a mono- or di-alkyl phosporic acid and a metal chelation collector selected from the group consisting of a 8-hydroyxquinoline substituted in the No. 7 position with a long chain aliphatic hydrocarbon radical and an oil-soluble 2-hydroxy benzophenoneoxime, a modifier which maintains solubility of the phosphoric acid and metal chelation collector and enhances phase disengagement, and a water immiscible carrier, the molar ratio of the 8-hydroxyquinoline and the phosphoric acid being between 1:1::1:4, respectively; wherein the ratio of extraction agent to water immiscible carrier is greater than 10:90;

said extraction performed at a volumetric ratio between said sulfuric acid and said extraction agent of between 4:1::1:4, and repeated to reduce substantially the contaminating iron impurities;

(e) filtering the product of step (d) through a carbon filter means to remove the residual extraction agent; and

(f) adding concentrated sulfuric acid to return the sulfuric acid concentration of the product of step (e) to a sulfuric acid concentration for use in new lead acid batteries; and

wherein the contaminating iron impurities are reduced to a level of no more than 20 parts per million in the final product of step (f).

2. A method of Claim 1 wherein said organophosphoric acid comprises di-2-ethyl hexyl phosphoric acid.

3. A method of Claim 1 wherein said modifier is selected from the group of alkyl phosphates and high molecular weight alcohols.

4. A method of Claim 3 wherein said modifier is tridecanol.

5. A method of Claim 1 wherein said water immiscible carrier comprises a hydrocarbon solvent in which both the chelating agent and the organophosphoric acid are soluble.

6. A method of Claim 5 wherein said water immiscible carrier is odorless mineral spirits.

7. A method of Claim 1 wherein said first filter means comprises a hydrolytic polypropylene plate.

8. A method of Claim 1 wherein said carbon filter comprises a packed column of granular activated carbon.

9. A method of Claim 1 wherein the contaminating elements are removed from the extraction agent by contacting said extraction agent with a strip acid with an acid concentration of between 30 and 50%.

10. A method of Claim 9 wherein the contaminating elements are removed from said extractant by cross flow contact with the strip acid.

11. A method of Claim 10 wherein said cross flow contact means comprises repeatedly contacting the extraction agent with progressively purer strip acid until the contaminating elements are adequately removed from the extraction agent.

12. A method of Claim 11 wherein after each treatment of the extraction agent with the strip acid, thereby decreasing the contaminant level in the extractant and increasing the contaminant level in the strip acid, the strip acid is fortified with concentrated acid and then employed again to remove contaminants from additional extraction agent containing contaminating elements.

13. A method of Claim 1 wherein said derivative 8-hydroxyquinoline is a 7-[3-(5, 5, 6, 7-tetramethyl-1-octenyl)]-8-hydroxyquinoline.

14. A method in accordance with Claim 1 wherein said dilution of the sulfuric acid comprises addition of water to achieve an acid concentration of substantially 15 to 18%.

15. A method for recycling contaminated sulfuric acid from lead acid batteries to reclaimed sulfuric acid for reuse in said batteries by removing contaminating iron impurities, the steps which comprise:

(a) diluting the contaminated sulfuric acid to a concentration between 150 and 230 grams per liter;

(b) filtering the sulfuric acid through a first filter means to remove solid impurities;

(c) oxidizing the sulfuric acid to assure that the iron contaminants are substantially in a ferric form;

(d) removing the iron contaminants from the sulfuric acid through liquid-liquid extraction using an extraction agent comprising mixture of a mono- or di-alkyl phosphoric acid and a metal chelation collector selected from the group consisting of a 9-hydroxyquinoline substituted in the No. 7 position with a long chain aliphatic hydrocarbon radical and an oil-soluble 2-hydroxy benzophenoneoxime, a modifier which maintains solubility of the phosphoric acid and the metal chelation collector and enhances phase disengagement, and a water immiscible carrier, the molar ratio of the 8-hydroxyquinoline and the phosphoric acid being between 1:1::1:4, respectively; wherein the ratio of extraction agent to water immiscible carrier is greater than 10:90;

said extraction performed at a volumetric ratio between said sulfuric acid and said extraction agent of between 4:1::1:4, and repeated until the contaminating iron impurities are substantially reduced;

(e) filtering the product of step (d) through a carbon filter means to remove the residual extraction agent;

(f) adding concentrated sulfuric acid to return the sulfuric acid concentration of the product of step (e) to a sulfuric acid concentration for use in new lead acid batteries, the final concentration of iron in the sulfuric acid being no more than 20 parts per million; and

(g) removing the contaminating elements from the extraction agent by contacting said extraction agent with a strip acid with an acid concentration of between 30 and 50%.

16. A method of Claim 15 wherein said derivative 8-hydroxyquinoline is a 7-[3-(5, 5, 6, 7-tetramethyl-1-octenyl)]-8-hydroxyquinoline.

17. A method of Claim 16 wherein said modifier is selected from the group of alkyl phosphates and high molecular weight alcohols.

18. A method of Claim 17 wherein said water immiscible carrier comprises a hydrocarbon solvent in which both the chelating agent and the organophosphoric acid are soluble.

19. A method of Claim 18 wherein the contaminating elements are removed from said extractant by cross flow contact with the strip acid.

20. A method of Claim 19 wherein said cross flow contact comprises repeatedly contacting the extraction agent with progressively purer strip acid until the contaminating elements are adequately removed from the extraction agent.

21. A method of Claim 20 wherein after each treatment of the extraction agent with the strip acid the strip acid is fortified with concentrated acid and then employed again to remove contaminants from additional extraction agent containing contaminating elements.

22. In a method for recycling contaminated sulfuric acid from lead acid batteries to reclaimed sulfuric acid for reuse in said batteries by removing contaminating iron impurities, the steps which comprise: (a) diluting the contaminated sulfuric acid to a concentration between 150 and 230 grams per liter; (b) filtering the sulfuric acid through a first filter means to remove solid impurities; (c) oxidizing the sulfuric acid to assure that the iron contaminants are substantially in a ferric form; (d) removing the iron contaminants from the sulfuric acid through liquid-liquid extraction using an extraction agent comprising mixture of a mono-or di-alkyl phosphoric acid and a metal chelation collector selected from the group consisting of a 8-hydroxyquinoline substituted in the No. 7 position with a long chain aliphatic hydrocarbon radical and an oil-soluble 2-hydroxy benzophenoneoxime, a modifier which maintains solubility

of the phosphoric acid and the metal chelation collector and enhances phase disengagement, and a water immiscible carrier, the molar ratio of the 8-hydroxyquinoline and the phosphoric acid being between 1:1::1:4, respectively; wherein the ratio of extraction agent to water immiscible carrier is greater than 10:90; said extraction performed at a volumetric ratio between said sulfuric acid and said extraction agent of between 4:1::1:4, and repeated until the contaminating iron impurities are substantially reduced; (e) filtering the product of step (d) to remove residual extraction agent; (f) adding concentrated sulfuric acid to return the sulfuric acid concentration of the product of step (e) to a sulfuric acid concentration for use in new lead acid batteries, the final concentration of iron in the sulfuric acid being no more than 20 parts per million; and (g) removing the contaminating elements from the extraction agent by contacting said extraction agent with a strip acid with an acid concentration of between 30 and 50%, the improvement which comprises:

(h) reusing the extraction agent to perform further extractions of ferric iron from contaminated sulfuric acid solution;

(i) treating the strip acid with means to reduce a portion of the removed ferric iron to ferrous iron;

(j) reusing the strip acid product of step (i), containing reduced iron, in step (g) to remove contaminating ferric iron from extraction agent.

23. The method of Claim 22 wherein the means to reduce the ferric iron to ferrous iron comprises

passing the strip acid through a cell having an anode compartment and a cathode compartment separated by means to prevent mixing of sulfuric acid between the anode and cathode compartments, and

applying electric current through the cell between the anode and the cathode to reduce the iron ions in the sulfuric acid in the cathode compartment of the cell.

24. The method of Claim 23 wherein the electric current applied through the cell is at least 1 amp at 3 volts.

25. The method of Claim 24 wherein the means to prevent mixing of sulfuric acid between the anode and cathode

compartments comprises a material selected from the group comprising ion exchange membrane, microporous film, microporous polyethylene diaphragm material, glass frit, and asbestos cloth material.

26. The method of Claim 23 wherein the means to reduce ferric iron to ferrous iron comprises passing the strip acid solution through a bed of activated carbon.

27. The method of Claim 23 wherein the contaminated sulfuric acid solution has a concentration of between 150 to 230 g/l and the strip acid has a concentration of approximately 400 to 500 g/l.

28. In a method for recycling contaminated sulfuric acid from lead acid batteries to reclaimed sulfuric acid for reuse in said batteries by removing contaminating iron impurities, the steps which comprise: (a) diluting the contaminated sulfuric acid to a concentration between 150 and 230 grams per liter; (b) filtering the sulfuric acid through a first filter means to remove solid impurities; (c) oxidizing the sulfuric acid to assure that the iron contaminants are substantially in a ferric form; (d) removing the iron contaminants from the sulfuric acid through liquid-liquid extraction using an extraction agent comprising mixture of a mono-or di-alkyl phosphoric acid and a metal chelation collector selected from the group consisting of a 8-hydroxyquinoline substituted in the No. 7 position with a long chain aliphatic hydrocarbon radical and oil-soluble 2-hydroxy benzophenoneoxime, a modifier which maintains solubility of the phosphoric acid and the metal chelation collector and enhances phase disengagement, and a water immiscible carrier, the molar ratio of the 8-hydroxyquinoline and the phosphoric acid being between 1:1::1:4, respectively; wherein the ratio of extraction agent to water immiscible carrier is greater than 10:90; said extraction performed at a volumetric ratio between said sulfuric acid and said extraction agent of between 4:1::1:4, and repeated until the contaminating iron impurities are substantially reduced; (e) filtering the product of step (d) to remove residual extraction agent; (f) adding concentrated sulfuric acid to return the sulfuric acid concentration of the product of step (e) to a sulfuric acid concentration for use in new lead acid batteries, the final concentration of iron in the

sulfuric acid being no more than 20 parts per million; and (g) removing the contaminating elements from the extraction agent by contacting said extraction agent with a strip acid with an acid concentration of between 30 and 50%, the improvement which comprises:

(h) reusing the extraction agent to perform further extractions of ferric iron from contaminated sulfuric acid solution;

(i) treating the strip acid with means to reduce a portion of the removed ferric iron to ferrous iron;

(j) reusing the strip acid product of step (i), containing reduced iron, in step (g) to remove contaminating ferric iron from extraction agent;

wherein the means to reduce the ferric iron to ferrous iron comprises

passing the strip acid through a cell having an anode compartment and a cathode compartment separated by means to prevent mixing of sulfuric acid between the anode and cathode compartments, and

applying electric current through the cell between the anode and cathode to reduce the iron ions in the sulfuric acid in the cathode compartment of the cell.

29. The method of Claim 28 wherein the cell is provided with intake means in the cell to receive contaminated strip acid containing iron substantially in a ferric form, and outlet means in the cell to deliver treated strip acid containing iron substantially in a ferrous form.

30. The method of Claim 28 wherein the means to prevent mixing of sulfuric acid between the anode and cathode compartments comprises a material selected from the group comprising ion exchange membrane, microporous film, microporous polyethylene diaphragm material, glass frit, and asbestos cloth material.

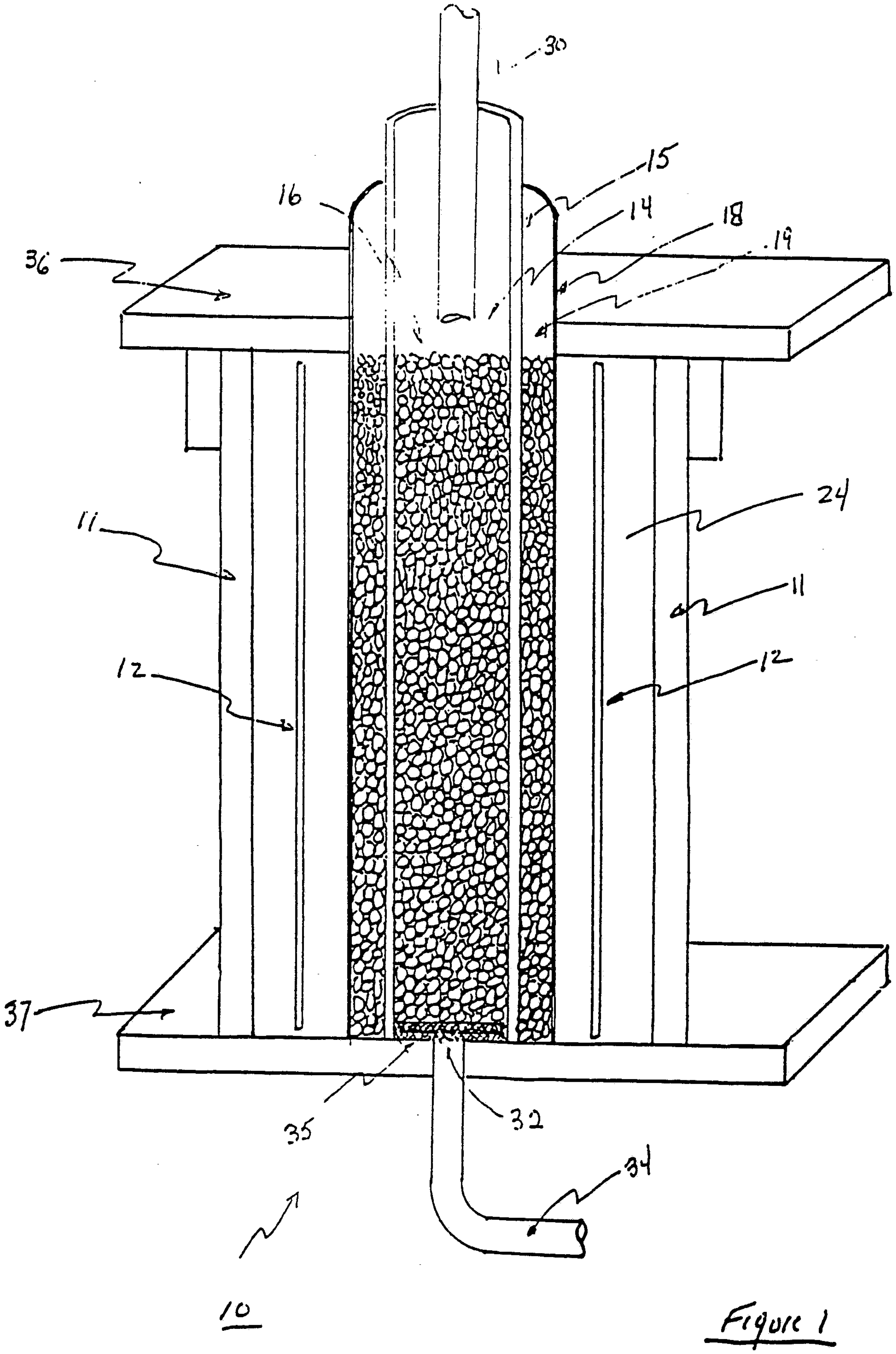

Figure 1

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/06772

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): C01B 17/90,B01D 11/00
US CL : 423/139,522,531; 429/49

## II. FIELDS SEARCHED

Minimum Documentation Searched [4]

| Classification System | Classification Symbols |
|---|---|
| US | 423/87,139,522,531; 429/49 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

## III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No. [18] |
|---|---|---|
| A | US, A, 900,454 (WADHAMS) 06 OCTOBER 1908 (SEE ENTIRE DOCUMENT) | ALL |
| A | US, A, 3,001,854 (KENWORTHY) 26 SEPTEMBER 1961 (SEE ENTIRE DOCUMENT). | ALL |
| A | US, A, 3,206,702 (GREENWOOD) 01 JULY 1963 (SEE ENTIRE DOCUMENT). | ALL |
| A | US, A, 3,428,449 (SWANSON) 18 FEBRUARY 1969 (SEE ENTIRE DOCUMENT). | ALL |
| A | US, A, 3,455,680 (ASHBROOK) 15 JULY 1969 (SEE ENTIRE DOCUMENT.) | ALL |
| A | US, A, 3,479,373 (ORLANDINI ET AL) 18 NOVEMBER 1969 (SEE ENTIRE DOCUMENT). | ALL |
| A | US, A, 3,540,860 (COCHRAN) 17 NOVEMBER 1970 (SEE ENTIRE DOCUMENT). | ALL |

* Special categories of cited documents: [15]

"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

"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

## IV. CERTIFICATION

| | |
|---|---|
| Date of the Actual Completion of the International Search [2]<br>05 JUNE 1991 | Date of Mailing of this International Search Report [2]<br>11 JUN 1991 |
| International Searching Authority [1]<br>ISA/US | Signature of Authorized Officer [20]<br>STEPHEN KULINCHAK |

Form PCT/ISA/210 (second sheet) (May 1986)

International Application No. PCT/US90/06772

**FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET**

| | | |
|---|---|---|
| A | US, A, 3,637,711 (BUDDE , JR. ET AL.) 25 MARCH 1968 (SEE ENTIRE DOCUMENT.) | ALL |
| A | US, A, 3,872,209 (HAZEN ET AL) 18 MARCH 1975 (SEE ENTIRE DOCUMENT) | ALL |
| A | US, A, 3,927,169 (GOREN ET AL) 16 DECEMBER 1975 (SEE ENTIRE DOCUMENT). | ALL |
| A | US, A, 3,950,488 (SKARBO ET AL.) 13 APRIL 1976 ( SEE ENTIRE DOCUMENT.) | ALL |

## V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE[1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter[1] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out[1], specifically:

3. ☐ Claim numbers___________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

## VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING[2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

International Application No. PCT/US90/06772

### III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No [18] |
|---|---|---|
| A | US, A, 3,966,569 (REINHARDT ET AL.)<br>29 JUNE 1976, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,002,564 (CARBONEL ET AL.)<br>11 JANUARY 1977, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,046,688 (CUNNINGHAM ET AL.)<br>6 SEPTEMBER 1977, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,061,564 (DE SCHEPPER ET AL.)<br>6 DECEMBER 1977, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,067,802 (CRONBERG ET AL.)<br>10 JANUARY 1978, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,082,832 (WATANABE ET AL.)<br>4 APRIL 1978, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,102,976 (HIEMELEERS ET AL.)<br>25 JULY 1978, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,210,530 (ETZEL ET AL.)<br>1 JULY 1980, SEE ENTIRE DOCUMENT | ALL |
| A | US,A4,383,104 (SASAKI ET AL.)<br>10 MAY 1983, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,414,183 (SASAKI ET AL.)<br>8 NOVEMBER 1983, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,444,666 (SATO)<br>24 APRIL 1984, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,499,058 (FITOUSSI ET AL.)<br>12 FEBRUARY 1985, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,501,666 (OGATA ET AL.)<br>26 FEBRUARY 1985, SEE ENTIRE DOCUMENT | ALL |
| A | US, A,4,559,216(NAGAI ET AL.)<br>17 DECEMBER 1985, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,582,691 (FUJIMOTO ET AL.)<br>15 APRIL 1986, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 4,628,011 (FELDMAN ET AL.)<br>9 DECEMBER 1986, SEE ENTIRE DOCUMENT | ALL |
| A | US, A, 3,841,916 (MARCHETTI)<br>15 OCTOBER 1974, SEE ENTIRE DOCUMENT | ALL |
| A | DE,A, 2,029,117<br>23 DECEMBER 1970, SEE ENTIRE DOCUMENT | ALL |

### III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category * | Citation of Document,[16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No [18] |
|---|---|---|
| A | DE, A, 2,515,862 28 OCTOBER 1976 (SEE ENTIRE DOCUMENT). | ALL |
| A | JP, A, 56-160,326 (NIPPON) 10 DECEMBER 1982 (SEE ENTIRE DOCUMENT) | ALL |
| A | JP, A, 59-162,138 (MITSUBISHI) 13 SEPTEMBER 1984 (SEE ENTIRE DOCUMENT). | ALL |
| A | JP, A, 52-43796 06 APRIL 1977 (SEE ENTIRE DOCUMENT). | ALL |
| A | DE, A, 1,161,432 16 JANUARY 1984 (SEE ENTIRE DOCUMENT). | ALL |
| A | SU, A, 452,524 (ISFARIWSK HYDROMETAL) 20 FEBRUARY 1973 (SEE ENTIRE DOCUMENT). | ALL |
| A | JP, A. 58-199,888 (NIPPON) 21 NOVEMBER 1983 (SEE ABSTRACT). | ALL |
| A | HYDROMETALLURGY, Vol. 12 (1981), DEMOPOULOS ET AL., "IRON(III) REMOVAL FROM BASE-METAL ELECTROLYTE SOLUTION BY SOLVENT EXTRACTION", PP. 299-315, SEE ENTIRE ARTICLE. | ALL |
| A | "DESCRIPTION AND OPERATION OF THE STONE & WEBSTER IONICS $SO_2$ REMOVAL AND RECOVERY PLANT", 07 NOVEMBER 1984 MELIERE ET AL., SEE ENTIRE ARTICLE. | ALL |
| A | INDUSTRIAL LABS, Vol. 45, No. 9, US, A, SEPTEMBER 1979 YUKHIM ET AL. "SEPARATION OF ANTIMONY AND ARSENIC BY EXTRACTION WITH DI-2-ETHYLHOXYLDITHIO-PHOSPHERIC ACID", PP. 979-981, SEE ENTIRE ARTICLE. | ALL |
| A | POLLUTION ENGINEERING, FEBRUARY 1988, BOYNTON "NEW LOW COST WASTEWATER RECOVERY PROCESS" page 34. | ALL |
| A | HARTUP, "COMPANY GETS THE LEAD OUT-AND MORE", DECEMBER 1979, SEE ENTIRE ARTICLE. | ALL |
| A | MASTERSON ET AL., "CHEMICAL PRINCIPLES 4TH EDITION, PUBLISHED 1977 BY W.B. SAUNDERS COMPANY (PHILADELPHIA), SEE P. 529. | ALL |