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RECOVERY OF METAL PHOSPHATES FROM INDUSTRIAL LIQUORS

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This application is a continuation-in-part of my patent application Ser. No. 49,430, filed Aug. 15, 1960, now abandoned.

This invention relates to a process for the recovery of chemicals from industrial liquors containing in solution acid salts of bivalent metals. The invention provides an improved process for recovering metal and acid values contained in industrial liquors and is based on the discovery that it is possible to precipitate and separately recover from industrial liquors, by the addition of phosphoric acid and other substances described below, complex phosphate compounds containing the bivalent cation of metal sought to be recovered from the liquors. In addition to the bivalent cation, the complex phosphate compounds also contain from about 4% to 8% by weight of ammonia (or an alkali metal equivalent of ammonia). The phosphate precipitate containing ammonia with this weight percentage range evinces so great an increase in filterability that the precipitated complexes can be readily and completely removed by normal separation processes.

The invention is applicable to the treatment of industrial liquors such as electrolytic liquors and pickling liquors which may contain the bivalent metals zinc, iron, magnesium, manganese, copper and cobalt. The liquors contain an inorganic acid such as sulfuric, hydrochloric or nitric acid and a salt of the bivalent metal; and if the acidity is too high, the liquors may first be neutralized with the bivalent metal or a compound of the bivalent metal such as zinc oxide or iron oxide when the bivalent metal is zinc or iron respectively.

The improved process of the invention is particularly suitable for use in the recovery of by-product acid and metal values contained in pickling or electrolytic liquors. For convenience and simplification of discussion the invention will be described with reference to the recovery of values from the liquors recovered from the electrolytic production of cadmium. It will be apparent from the following discussion that the process is equally applicable to the recovery of acid and metal values from other industrial liquors. The chief components of a typical electrolyte liquor are:

Sulfuric acid (H_2SO_4)	19.2
Zinc (as $ZnSO_4$)	2.4
Iron (as $FeSo_4$)	0.7
Manganese (as $MnSo_4$)	0.1

The electrolytic liquors containing sulfuric acid in such concentrations are preferably substantially neutralized by addition of zinc or a zinc compound such as zinc oxide, zinc carbonate, or zinc sulfide, and like zinc-containing materials. The neutralizing can be represented by the equation:

$$H_2SO_4+ZnO\rightarrow ZnSO_4+H_2O$$

Electrolytic liquors may contain sulfuric acid, hydrochloric acid or nitric acid and when the liquor contains a zinc salt the liquor may be neutralized according to the following equations:

ZINC

Group I

$$H_2SO_4+Zn\rightarrow ZnSO_4+H_2$$
$$2HCl+Zn\rightarrow ZnCl_2+H_2$$
$$8HNO_3+3Zn\rightarrow 3Zn(NO_3)_2+2NO+4H_2O$$

Group II

$$H_2SO_4+ZnO\rightarrow ZnSo_4+H_2O$$
$$2HCl+ZnO\rightarrow ZnCl_2+H_2O$$
$$2HNO_3+ZnO\rightarrow Zn(NO_3)_2+H_2O$$

Group III

$$H_2SO_4+ZnCO_3\rightarrow ZnSO_4+H_2O+CO_2$$
$$2HCl+ZnCO_3\rightarrow ZnCl_2+H_2O+CO_2$$
$$2HNO_3+ZnCO_3\rightarrow Zn(NO_3)_2+H_2O+CO_2$$

Group IV

$$H_2SO_4+ZnS_2\rightarrow ZnSO_4+H_2S+S$$
$$2HCl+ZnS_2\rightarrow ZnCl_2+H_2S+S$$
$$2HNO_3+ZnS_2\rightarrow Zn(NO_3)_2+H_2S+S$$

Group V

$$2H_2SO_4+FeZn\rightarrow FeSO_4+ZnSO_4+2H_2O$$
$$4HCl+FeZn\rightarrow FeCl_2+ZnCl_2+4H$$
$$2HNO_3+FeZn\rightarrow 3Zn(NO_3)_2+3Fe(NO_3)_2+4NO+8H_2O$$

When the liquor contains other salts such as the above salts of iron, magnesium, manganese, cobalt or copper then the neutralizing can be effected by similar reactions by substituting in the above reactions Fe, Mg, Mn, Co and Cu for Zn.

Other valences of iron, manganese, cobalt and copper, with required adjustments to quantitatively balance them chemically, are intended to be disclosed by the equations listed.

Iron-zinc (Fe-Zn), magnesium (Mg), manganese (Mn), cobalt (Co), and copper (Cu) substitutions in Group V are intended to disclose all combinations of the metals with each other.

It is not always necessary to resort to the above initial neutralizing. In case of the iron pickle liquor the chief components of which may, in a typical example, be

	Percent
Sulfuric acid (H_2SO_4)	2.0
Ferrous sulfate ($FeSO_4$)	19.2

one may preferably entirely forego the first neutralizing step and proceed directly to final substantially entire neutralization of the acid content by phosphoric acid and alkali cation combinations containing at least one of the group comprising ammonia, potassium, sodium, and lithium, to precipitate zinc phosphates containing from about 4%–8% alkali cation in the form of the alkali cation iron phosphates to tremendously increase their filterability.

The following examples illustrate the critical amounts of ammonia in forming zinc phosphate complexes to achieve rapid filtration and the recovery of the complex.

To one portion of the substantially neutralized solution of zinc sulfate, add phosphoric acid and ammonia, while agitating, in quantities sufficient to bring the final pH of the mixture to between 6.2 to 7.2. This results in the precipitation of a zinc phosphate complex according to the equation:

$$ZnSO_4+H_3PO_4+3NH_3\rightarrow (NH_4)_2SO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

Under these conditions the precipitated zinc phosphate complex contains 3.3% ammonia present in the form of ammonium zinc phosphates constituting about 34% by weight of the precipitated complex of zinc and ammonium phosphates.

To a second portion of the substantially neutralized solution add monoammonium phosphate and ammonia, while agitating, in quantities sufficient to bring the final pH of the mixture to between 6.2 and 7.2. This results in the precipitation of a zinc phosphate complex according to the equation:

$$ZnSO_4+NH_4H_2PO_4+2NH_3\rightarrow (NH_4)_2SO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

Under these conditions the precipitated zinc phosphate complex contains 5.2% ammonia, present in form of ammonium zinc phosphates constituting about 54% by weight of the precipitated complex of zinc and ammonium phosphates.

To a third portion of the substantially neutralized solution add diammonium phosphate and ammonia, while agitating in quantities sufficient to bring final pH of the mixture to between 6.2 and 7.2. This results in the precipitation of a zinc phosphate complex according to the equation:

$$ZnSO_4+(NH_4)_2HPO_4+NH_3\rightarrow(NH_4)_2SO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

Under these conditions the precipitated zinc phosphate complex contains 6.7% ammonia, present in form of ammonium zinc phosphates constituting about 67% by weight of the precipitated complex of zinc and ammonium phosphates.

To a fourth portion of the substantially neutralized solution add three times the amount of the diammonium phosphate used in the example next above. In addition, add ammonia and agitate while adding same. The quantities of diammonium phosphate and ammonia added are such as to bring final pH of the mixture to between 6.2 and 7.2. This results in the precipitation of a zinc phosphate complex according to the following equation:

$$ZnSO_4+3(NH_4)_2HPO_4+NH_3\rightarrow(NH_4)_2SO_4+(NH_4)_2HPO_4+NH_4H_2PO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

Under these conditions the precipitated zinc phosphate complex contains 8.1% ammonia, present in the form of ammonium zinc phosphates constituting about 81% by weight of the precipitated complex of zinc and ammonium phosphates.

Phosphoric acid may be added to the electrolyte liquor prior to or in conjunction with the source of ammonia. Otherwise addition of ammonia in quantity needed to substantially complete the reactions will hydrolyze or precipitate the hydroxides of zinc instead of the mixed complexes of zinc and ammonium phosphates. This will have an adverse effect upon the filterability and therefore, separability, of the phosphate precipitate.

Each of the precipitates in the four examples were formed at about pH 7 and were recovered by filtration as follows: The homogenous mixture of precipitate and mother liquor was added to a one-half inch I.D. glass tube 24 inches long and fitted with a No. 0 rubber stopper containing a one-tenth inch center hole covered by a No. 40 whatman filter paper cut to the exact size of the small end of the stopper and fastened securely to the flat edges thereof by insoluble glue. Results were:

Example	Ammonia (percent by weight present in the complex phosphate precipitate)	Time (in minutes) required to filter 25 cc. of treated liquor
1	3.3	2,160
2	5.2	93
3	6.7	180
4	8.1	215

The foregoing table shows that the amount of ammonia in the ammonium zinc phosphate complex greatly affects the rate of filterability. As shown, the filtration rate for the complex containing 3.3% of ammonia has an impractically long filtration rate.

My process of treating industrial liquor containing a bivalent metal compound comprises mixing with said liquor, phosphoric acid and ammonia in combinations to substantially entirely neutralize the liquor and precipitate a metal salt of phosphate containing from about 4% to about 8% ammonia, present in the precipitate in the form of ammonium metal phosphate. The precipitate has very good filterability and is efficiently filtered from its mother liquor.

The above illustrative examples may be carried out by treating industrial liquors containing zinc salts of sulfates, chlorides or nitrates according to the following reactions:

$$ZnSO_4+H_3PO_4+3NH_3\rightarrow(NH_4)_2SO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$ZnCl_2+H_3PO_4+3NH_3\rightarrow2NH_4Cl+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$Zn(NO_3)_2+H_3PO_4+3NH_3\rightarrow2NH_4NO_3+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$ZnSO_4+NH_4H_2PO_4+2NH_3\rightarrow(NH_4)_2SO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$ZnCl_2+NH_4H_2PO_4+2NH_3\rightarrow2NH_4Cl+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$Zn(NO_3)_2+NH_4H_2PO_4+2NH_3\rightarrow2NH_4NO_3+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$ZnSO_4+(NH_4)_2HPO_4+NH_3\rightarrow(NH_4)_2SO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$ZnCl_2+(NH_4)_2HPO_4+NH_3\rightarrow2NH_4Cl+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$Zn(NO_3)_2+(NH_4)_2HPO_4+NH_3\rightarrow2NH_4NO_3+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$ZnSO_4+3(NH_4)_2HPO_4+NH_3\rightarrow(NH_4)_2SO_4+(NH_4)_2HPO_4+NH_4H_2PO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$ZnCl_2+3(NH_4)_2HPO_4+NH_3\rightarrow2NH_4Cl+(NH_4)_2HPO_4+NH_4H_2PO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

$$Zn(NO_3)_2+3(NH_4)_2HPO_4+NH_3\rightarrow2NH_4NO_3+(NH_4)_2HPO_4+NH_4H_2PO_4+[Zn_3(PO_4)_2\cdot NH_4ZnPO_4]$$

It is to be understood that this invention contemplates the use of other materials than those mentioned in the above equation—for example (1) compounds having a cation of the group consisting of potassium, sodium and lithium, such as KOH, NaOH and LiOH, may be used in place of NH_3; (2) compounds having $K+$, $Na+$, or $Li+$ cations may be substituted for the NH_4+ cation; and (3) compounds having a cation of the group consisting of iron, manganese, magnesium, cobalt and copper may be used in place of the zinc.

By the present invention neutralization and filtration are continually occurring so that no time or labor is lost in the handling and transporting of liquor. In addition, a given volume of liquor will be completely treated generally in less than fifteen minutes as compared to the usual one to two hours required for treatment by former practices involving substantially complete ammoniation of the normal metal phosphate precipitates. This time saving is partly brought about by effective mechanical agitation and neutralization operations but mostly by the fact that the precipitated metal phosphate complexes need only be ammoniated to the extent of containing from about 4% to 8% of ammonia, present in the form of ammonium metal phosphates.

The continuous process of the present invention for recovery of precipitated zinc phosphate complex is advantageously carried out as follows in treating, for example, an electrolytic liquor containing a zinc salt and sulfuric acid. The industrial liquor is substantially completely neutralized initially by reacting the sulfuric acid with a zinc compound such as zinc oxide to form zinc sulfate.

To the neutralized liquor containing zinc sulfate in solution, phosphoric acid, ammonia and air are added and thoroughly intermixed in a reactor vessel by means of a mechanical agitator to insure complete reaction between the zinc sulfate and the phosphoric acid and ammonia combinations. The ammonia or ammonia-containing compound is added in such an amount that the resulting zinc ammonium phosphate complex contains 4 to 8% of ammonia. The liquor containing the zinc salt and the phosphoric acid and the ammonia or ammonia-containing compound are conducted into the reactor separately in such manner that the phosphoric acid is dis-

charged at a level below the liquor and the ammonia is discharged at a level below the phosphoric acid. This practice insures efficient formation of ammonium phosphates so that reaction between the zinc salt and the ammonia and phosphoric acid combinations is substantially by ion exchange between the zinc salts and ammonium phosphate thereby minimizing precipitation by ammonia of zinc as oxide.

The filterability of the liquor is extremely poor when the complex zinc phosphate precipitate contains only about 3% ammonia. This indicates that the precipitates at this degree of ammoniation are in colloidal states which makes them very difficult to filter from their mother liquor. It has been found that as the percentage of ammoniation is increased substantially beyond 3% the filterability of the precipitate increases so greatly that the zinc precipitates can be readily and completely removed by normal separating processes. The degree of excellent filterability lies in the range of about 4% to about 8% ammonia, present in the form of ammonium zinc phosphates.

Air may be used for agitation and oxidation purposes. It is preferred to introduce the air beneath the circular path of the rotating paddles of a mechanical agitator but above the entering points of the phosphoric acid and ammonia so that the air, acid and ammonia will be thrown outwardly by the agitator and tend to disperse in finely divided particles effectively promoting formation of zinc ammonium phosphates. Atomization causes all reactants to be distributed equally throughout the entire mass so that rates of reaction are increased and if precipitation occurs to some extent in the form of lower valency metal oxides these are substantially oxidized and the filterability of the precipitated complex is further improved.

I claim:

1. A process for recovering a complex having improved filterability from an industrial liquor containing an inorganic salt of the group consisting of sulfuric, hydrochloric and nitric acid, and a metal cation of the group consisting of zinc, iron, magnesium, manganese, cobalt and copper, said process comprising concurrently adding to the industrial liquor

(A) a substance selected from the group consisting of ammonia, a potassium compound, a sodium compound and a lithium compound, or mixtures thereof, and

(B) a material selected from the group consisting of

(1) an inorganic phosphate salt having a cation selected from the group consisting of $K+$, $Na+$, $Li+$ and NH_4+, or mixtures thereof, and

(2) a substance which forms said inorganic phosphate salt,

the amount of (B) being in a quantity to combine with the metal cation in the industrial liquor, the amount of (A) being in a quantity in excess of that required to combine with the sulfuric, hydrochloric or nitric acid in the industrial liquor, and continuing to add (A) until the pH of the liquor attains a value of 6.2 to 7.2, thus precipitating a complex characterized by including a phosphate salt having a cation of the group consisting of zinc, iron, magnesium, manganese, cobalt and copper or mixtures thereof and a phosphate salt having a cation of the group consisting of potassium, sodium, lithium and ammonium or mixtures thereof, said complex having an ammonia content of from 4 to 8% by weight or having equivalent weight contents of potassium, sodium and lithium, whereby the filterability of the complex is improved, and filtering said liquor in order to separate the complex therefrom.

2. The process of claim 1 wherein (A) is added subsequent to the addition of (B).

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