



PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to the Extraction of Metal Values

We, THORIUM LIMITED, a British Company, of 9 Basingall Street, London, E.C.2., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the extraction of metal values from aqueous media containing such values.

The invention consists in a method of extracting metal values from an aqueous medium containing at least one metal value in solution or suspension, the metal of this value being less basic than an alkaline earth metal (including Magnesium), in which the aqueous medium is contacted with a solution of an alkaline earth metal naphthenate in an inert solvent which is substantially immiscible with the aqueous medium.

Suitable inert solvents include liquid aromatic hydrocarbons such as benzene, toluene or xylene, or mixtures of aliphatic hydrocarbons containing up to 10% of aromatic hydrocarbons, such as white spirit and kerosene. Kerosene is the preferred solvent.

The alkaline earth metal naphthenate solution may preferably be prepared according to the process disclosed in British Specification No. 915,428, i.e. by reacting a solution of naphthenic acid in the inert organic solvent with an aqueous solution or suspension of the appropriate alkaline earth metal base. For instance, an aqueous slurry of magnesium oxide or calcium hydroxide may be reacted with a solution of naphthenic acid in kerosene. It may be necessary to separate the desired naphthenate solution by means of a centrifuge. Thus a magnesium naphthenate solution prepared by stirring a one molar kerosene solution of naphthenic acid with an aqueous slurry containing excess magnesium oxide could only be separated in a centri-

fuge, and the excess magnesium oxide still occluded considerable amounts of the organic phase. The magnesium naphthenate solution formed readily extracted copper from a copper sulphate solution. The maximum loading possible was 11.6 g/l. Cu indicating that 36% of the naphthenic acid had reacted to form magnesium naphthenate. A preferred method of preparing the magnesium naphthenate solution is to use a solution of magnesium oxide in ammonium chloride solution. The magnesium oxide in this solution reacts as magnesium hydroxide and readily reacts with a kerosene solution of naphthenic acid with good separation of the two phases on standing. A magnesium naphthenate solution prepared from molar naphthenic acid could be loaded with a maximum of 21.0 g/l Cu which is equivalent to 66 per cent conversion of the naphthenic acid to magnesium naphthenate. The solution contained 0.33 molar magnesium naphthenate and was used in the series of extraction tests described in the examples.

A solution of calcium naphthenate was prepared by mixing a kerosene solution of naphthenic acid with an aqueous slurry of calcium hydroxide. Molar naphthenic acid yielded a very viscous solution which could not be separated from the aqueous phase, but 0.5 M naphthenic acid gave a mobile solution which separated readily in a centrifuge. On shaking this calcium naphthenate solution with an aqueous solution of copper sulphate an intractable emulsion was obtained which could however be separated in a centrifuge. The separated aqueous phase contained the precipitated calcium sulphate with a large amount of occluded organic phase. Calcium naphthenate is unsuitable for a continuous process using solutions of metal sulphates but with chloride solutions a continuous process can be worked. Magnesium naphthen-

ate is suitable for a continuous process with chlorides and even with sulphates.

Other possible methods of preparing the alkaline earth naphthenate solution in the inert solvent include forming the alkaline earth naphthenate by double decomposition of an alkaline earth metal salt, for instance magnesium sulphate with sodium naphthenate and extracting the alkaline earth naphthenate with the inert organic solvent.

The concentration of naphthenic acid in the solutions in inert organic solvents used to form the reagent is, apart from considerations of solubility, a matter of practical convenience. At higher concentrations the metal naphthenate solutions tend to be viscous and not to give good phase separation. It is generally preferred not to use alkaline earth metal naphthenate solutions stronger than 0.5. M.

Although the method of the invention is generally applicable to the extraction of metals which form naphthenates which are readily soluble in the inert organic solvent and substantially insoluble in water (other than the alkaline earth metals themselves), its use in the separation of metals depends on the difference in stability of the respective naphthenates. It is found that by using the stoichiometric amount of the alkaline earth metal naphthenate appropriate to the relatively more stable metal (as regards naphthenate formation) the latter can be extracted substantially quantitatively leaving in the aqueous raffinate the metal or metals which form the relatively less stable naphthenates. This is therefore a further preferred feature of the process.

The method of the invention is particularly applicable to the separation of copper from cobalt, nickel, cadmium, lead, zinc and/or tin.

The solutions of naphthenates obtained by the process of the invention may be stripped of the desired metal values by contacting with mineral acids to give an aqueous solution of the metal values and a solution of naphthenic acid in the inert solvent. The alkaline earth naphthenate may be regenerated by reacting this naphthenic acid solution with an alkaline earth metal base for instance, by the methods set forth above.

A flow sheet of a system for regeneration which can be used with magnesium naphthenate is shown in the drawing accompanying the provisional specification. While fresh supplies of magnesium oxide are required for the regeneration of the reagent, in this embodiment the ammonium chloride used for dissolving the magnesium oxide is recycled and is not therefore consumed during the process.

However, precautions should be taken to prevent the loss of ammonia by volatilisation; in practice this can be readily accom-

plished by the use of closed vessels for mixing and settling. The loss of ammonia by the formation of ammonium naphthenate, which is partially soluble in kerosene, is avoided by the fact that although the pH of MgO in ammonium chloride is 8.4, the equilibrium pH, that is, the pH of the solution after contacting with the naphthenic acid/kerosene solution is 6.4. The formation of ammonium naphthenate only becomes detectable at an equilibrium pH of 7.0.

The process of extraction is substantially independent of the pH of the aqueous medium containing the metal values. It can be applied, for instance, to solutions of the sulphates of metals at their natural pH as well as to solutions of lower pH.

It is uneconomic to carry out extractions from solutions containing free acid because in such cases the magnesium naphthenate reagent will be consumed in neutralising the free acid and an excess of the reagent will be required to carry out the desired metal extraction.

Since it is not necessary to raise the pH as in the naphthenic acid process disclosed in British Specification No. 915,428, the use of expensive alkaline reagents, especially ammonia is avoided. The present process is therefore suitable for use as an alternative to that described in British Specification No. 915,428 in territories where cheap supplies of magnesite are available. The use of magnesium naphthenate in the present process also has the advantage that it avoids the formation of basic sulphates which may be formed with certain metals at high pH when employing the process of British Specification No. 915,428.

The invention is further illustrated by the following examples:—

EXAMPLE I

A 0.33 molar solution of magnesium naphthenate in kerosene prepared as described above was shaken with twice its volume of an aqueous solution of copper and nickel, the two phases allowed to settle and the organic phase stripped with dilute sulphuric acid. The copper and nickel content of the raffinate and the acid extract were determined and the metal content of the organic phase calculated. The results are given in Table I. It will be seen that when the amount of copper is insufficient to react with all the magnesium naphthenate (test No. 1) more nickel was extracted into the organic phase than when the copper was equivalent to that extractable (test No. 2), while when copper is in excess (tests Nos. 3 and 4), some remains in the raffinate. The desirability of using an amount of magnesium naphthenate equivalent to the copper, so as to attain good separation of the latter from nickel is thus demonstrated.

Test No.	Ratio organic aqueous	Feed Solution		pH		Organic phase		Raffinate		% Extraction by organic	
		Cu g/l	Ni g/l	Feed	Raffinate	Cu g/l	Ni g/l	Cu g/l	Ni g/l	Cu	Ni
1	0.5	10.06	6.11	4.00	5.55	20.10	0.56	0.01	5.45	99.9	4.5
2	0.5	10.48	6.11	4.15	5.05	20.90	0.07	0.03	5.04	99.7	1.1
3	0.5	10.68	5.85	4.15	4.75	20.96	0.04	0.20	5.81	98.1	0.6
4	0.5	10.80	5.85	4.15	4.75	20.96	0.036	0.32	5.81	97.0	0.6

EXAMPLE II

Copper/nickel solutions were shaken with equal volumes of magnesium naphthenate; the separated organic phase was stripped with dilute sulphuric acid, the copper and naphthenate equivalent to the copper and nickel content determined and the metal content of the nickel extract calculated. The phase was stripped with dilute sulphuric acid, the copper and nickel content of the final aqueous raffinate was also determined. The results are given in Table 2.

TABLE 2, Copper and Nickel Extractions with Magnesium Naphthenate

Test No.	Ratio organic aqueous	Feed Solution		pH		Copper Extract		Nickel extract		Nickel raffinate		% Distribution						
		Cu g/l	Ni g/l	Feed	Cu raff	Ni raff	Cu g/l	Ni g/l	Cu g/l	Ni g/l	Cu g/l	Ni g/l	Cu Extract	Ni Extract	Ni Raffinate	Cu Ni		
5	1.0	20.9	17.7	4.1	5.20	6.60	20.7	0.4	0.5	16.6	0.0	0.6	97.7	2.6	2.3	94.0	0.0	3.4
6	1.0	20.7	16.6	4.2	5.40	6.75	20.4	0.3	0.1	16.4	0.0	0.3	99.5	1.7	0.5	96.6	0.0	1.7
7	1.0	23.1	19.3	3.85	5.40	6.75	22.8	0.2	0.1	18.4	0.0	0.6	99.6	1.0	0.4	95.9	0.0	3.1
8	0.83	22.4	20.3	4.20	5.25	7.20	23.8	0.3	0.2	24.5	0.05	0.6	99.0	1.2	0.8	96.5	0.2	2.3

Tests Nos. 5 and 6 were carried out using the same magnesium naphthenate solution as in Example I. Test No. 7 was carried out using a solution in which 73% naphthenic acid had been converted to magnesium naphthenate the solution of which was 0.364 M; the figures for the solution used in Test No. 8 were: 85%, 0.424 M. Both the latter solutions were prepared by extracting MgO/
 10 NH_4Cl solutions with 1M naphthenic acid in kerosene.

WHAT WE CLAIM IS:—

1. A method of extracting metal values from an aqueous medium containing at least
 15 one metal value in solution or suspension, the metal of this value being less basic than an alkaline earth metal (including magnesium), in which the aqueous medium is contacted with a solution of an alkaline earth metal
 20 naphthenate in an inert solvent which is substantially immiscible with the aqueous medium.
2. A method as claimed in claim 1, in which the solvent is an aromatic hydrocarbon or a mixture of an aliphatic hydrocarbon
 25 and up to 10% of an aromatic hydrocarbon.
3. A method as claimed in claim 2, in which the solvent is kerosene.
4. A method as claimed in claim 1, 2
 30 or 3, in which the alkaline earth metal naphthenate solution is prepared by double decomposition of an alkaline earth salt with an alkali metal naphthenate and extracting the alkaline earth naphthenate with the inert
 35 organic solvent.
5. A method as claimed in claim 1, 2 or 3, in which the alkaline earth metal naphthenate solution is prepared by reacting a solution of naphthenic acid in the inert
 40 organic solvent with an aqueous solution or suspension of the alkaline earth metal base.
6. A method as claimed in claim 5, in which an aqueous slurry of magnesium oxide or calcium hydroxide is used.
7. A method as claimed in claim 6, in
 45 which a slurry of calcium hydroxide is used and contracted with kerosene as the organic solvent.
8. A method as claimed in claim 6 or 7,

in which the naphthenate solution produced is separated in a centrifuge. 50

9. A method as claimed in claim 5, in which a solution of magnesium oxide in ammonium chloride solution is used and contacted with kerosene as the organic solvent. 55

10. A method as claimed in any one preceding claim, in which the alkaline earth metal naphthenate solution used to extract the metal values is less than 0.5 M.

11. A method as claimed in any one preceding claim, in which the aqueous medium contains more than one metal value in solution, and the stoichiometric amount of alkaline earth metal naphthenate to correspond to the metal forming the relatively more stable naphthenate is used. 60 65

12. A method as claimed in any one preceding claim applied to the separation of copper from cobalt, nickel, cadmium, lead, zinc and/or tin. 70

13. A method as claimed in any one preceding claim in which the solution of naphthenate produced after contacting with the metal value is contacted with a mineral acid to give an aqueous solution of any metal value present and regenerate naphthenic acid in the inert solvent. 75

14. A method as claimed in claim 13, in which naphthenic acid is converted to alkaline earth metal naphthenate by the steps as set forth in any of claims 5 to 9. 80

15. A method as claimed in claim 14 when carried out as a continuous process.

16. A method as claimed in claim 15, in which sulphates of the metal values are contacted with calcium naphthenate. 85

17. A method as claimed in claim 15, in which sulphates or chlorides of the metal value are contacted with magnesium naphthenate. 90

18. A method of extracting metal values substantially as herein described with reference to Example 1 or Example 2.

19. Metal values extracted by the method as claimed in any one preceding claim. 95

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- Tests Nos. 5 and 6 were carried out using the same magnesium naphthenate solution as in Example I. Test No. 7 was carried out using a solution in which 73% naphthenic acid had been converted to magnesium naphthenate the solution of which was 0.364 M; the figures for the solution used in Test No. 8 were: 85%, 0.424 M. Both the latter solutions were prepared by extracting MgO/ NH_4Cl solutions with 1M naphthenic acid in kerosene.

WHAT WE CLAIM IS:—

1. A method of extracting metal values from an aqueous medium containing at least one metal value in solution or suspension, the metal of this value being less basic than an alkaline earth metal (including magnesium), in which the aqueous medium is contacted with a solution of an alkaline earth metal naphthenate in an inert solvent which is substantially immiscible with the aqueous medium.
2. A method as claimed in claim 1, in which the solvent is an aromatic hydrocarbon or a mixture of an aliphatic hydrocarbon and up to 10% of an aromatic hydrocarbon.
3. A method as claimed in claim 2, in which the solvent is kerosene.
4. A method as claimed in claim 1, 2 or 3, in which the alkaline earth metal naphthenate solution is prepared by double decomposition of an alkaline earth salt with an alkali metal naphthenate and extracting the alkaline earth naphthenate with the inert organic solvent.
5. A method as claimed in claim 1, 2 or 3, in which the alkaline earth metal naphthenate solution is prepared by reacting a solution of naphthenic acid in the inert organic solvent with an aqueous solution or suspension of the alkaline earth metal base.
6. A method as claimed in claim 5, in which an aqueous slurry of magnesium oxide or calcium hydroxide is used.
7. A method as claimed in claim 6, in which a slurry of calcium hydroxide is used and contracted with kerosene as the organic solvent.
8. A method as claimed in claim 6 or 7, in which the naphthenate solution produced is separated in a centrifuge.
9. A method as claimed in claim 5, in which a solution of magnesium oxide in ammonium chloride solution is used and contacted with kerosene as the organic solvent.
10. A method as claimed in any one preceding claim, in which the alkaline earth metal naphthenate solution used to extract the metal values is less than 0.5 M.
11. A method as claimed in any one preceding claim, in which the aqueous medium contains more than one metal value in solution, and the stoichiometric amount of alkaline earth metal naphthenate to correspond to the metal forming the relatively more stable naphthenate is used.
12. A method as claimed in any one preceding claim applied to the separation of copper from cobalt, nickel, cadmium, lead, zinc and/or tin.
13. A method as claimed in any one preceding claim in which the solution of naphthenate produced after contacting with the metal value is contacted with a mineral acid to give an aqueous solution of any metal value present and regenerate naphthenic acid in the inert solvent.
14. A method as claimed in claim 13, in which naphthenic acid is converted to alkaline earth metal naphthenate by the steps as set forth in any of claims 5 to 9.
15. A method as claimed in claim 14 when carried out as a continuous process.
16. A method as claimed in claim 15, in which sulphates of the metal values are contacted with calcium naphthenate.
17. A method as claimed in claim 15, in which sulphates or chlorides of the metal value are contacted with magnesium naphthenate.
18. A method of extracting metal values substantially as herein described with reference to Example 1 or Example 2.
19. Metal values extracted by the method as claimed in any one preceding claim.

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