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# PATENT SPECIFICATION (11) 1 593 289

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(19)

## (54) RECOVERY OF GALLIUM FROM AQUEOUS SOLUTION

(71) We, RHONE-POULENC INDUSTRIES, a French body corporate, of 22, avenue Montaigne, 75 Paris (8), France, 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:—

The invention concerns an improvement to the method of recovering gallium from very basic solutions by liquid/liquid extraction described and claimed in the specification of our copending application No. 29103/75 (1 513 398).

This application describes and claims a process for recovering the gallium present in a strongly basic aqueous solution, particularly sodium aluminate solutions obtained from the Bayer alumina process, that comprises liquid/liquid extraction by means of an organic phase comprising an extracting agent consisting essentially of a water-insoluble substituted hydroxyquinoline and a water-immiscible organic solvent, and removal of the gallium from the organic phase by means of a strong acid. The term "strongly basic" is defined as meaning that the solution has a pH of at least 14, and this definition is adopted in the present specification. The gallium recovery process described in this application includes a stage of extraction proper and a stage where the solvent is regenerated and the gallium recovered by means of strong acids. There are two preferred methods of carrying out the process, according to the acid used and its concentration in the stage where the solvent charged with gallium is regenerated.

The first method, which can use any strong acid, comprises first treating the organic phase with a dilute solution of the strong acid of dilution such that the acid strips only sodium and aluminium from the organic phase, and then treating the stripped organic phase with a moderately dilute solution of the strong acid, the dilution of this second solution being such that the acid extracts the gallium from the organic phase. The dilution in the first stage is preferably from 0.4*n* to 0.8*n*, particularly about 0.5*n* or 0.6*n*; the dilution in the second stage is preferably over 1*n*, particularly about 2*n*. This two-stage recovery has the additional advantage of eliminating a certain number of metallic impurities, such as zinc, lead and cobalt, from the aluminate solutions. Such impurities may pass into the organic phase but will pass back into the aqueous phase when the complex-forming agent receives its first treatment with a dilute acid.

The second method makes use of the formation of anionic complexes of gallium with hydrochloric acid as well as with other acids such as hydrobromic acid. In this method, the organic phase containing the gallium-hydroxy-quinoline complex is first treated with a concentrated strong acid, the concentration being such that there is produced a complex of gallium with the anion of the acid, the complex being soluble in the organic phase, and the aluminium and sodium are consequently stripped from the organic phase by the acid, and the organic phase is then treated with a moderately dilute solution of the acid, whereby the gallium is extracted from the organic phase. When hydrochloric acid, which is the preferred acid, is used in the first step, its concentration should be at least 5*n*; when it is used in the second step, its concentration should be about 1.5*n* or 2*n*. Hydrobromic acid is also quite suitable. In general, the concentration of the concentrated solution is preferably from 5*n* to 8*n* and that of the dilute solution from 1.3*n* to 2.2*n*.

Moreover, if the production of gallium of a lower degree of purity is desired, it is possible to operate by putting the aqueous solution into contact with a water-insoluble substituted hydroxyquinoline in solution in a water-insoluble halogenated

or non-halogenated aliphatic or aromatic hydrocarbon in such a way that the gallium and a certain quantity of sodium and aluminium transfer from the aqueous phase to the organic phase; separating the organic phase from the aqueous phase; putting the organic phase into contact with an aqueous solution of an acid to extract the sodium, aluminium and gallium from the organic phase; separating the aqueous and organic phases; and recovering the gallium, sodium and aluminium.

The acid solutions used are preferably either solutions of sulphuric acid or nitric acid in a concentration of higher than 1.6*n*, or hydrochloric acid or hydrobromic acid in a concentration of from 1.3*n* to 2.2*n*.

In the gallium extracting stage described in this application it may be advantageous to add substances with an alcohol funcation, e.g. heavy alcohols such as N-decanol and isodecanol, various heavy phenols, or other solvating compounds, e.g. certain phosphoric esters such as tri-butyl phosphate, in the organic extraction phase in known manner.

The concentration of substituted hydroxyquinoline in the organic phase need not be very high, for even a concentration as low 2% gives good extraction of gallium, due to the far greater affinity of these chelating agents for gallium than for aluminium and sodium; in practice, however, concentrations in the order of 10% are more favourable and enable the majority of the gallium to be extracted.

Furthermore, although temperature is not a critical parameter for obtaining good results by the method described in the said application, it is advantageous for the extraction stage to be carried out at a fairly high temperature, in practice not exceeding 100°C and preferably from 50 to 80°C. It may be added that in industrial practice the solutions generally treated are aluminate solutions from the Bayer process, particularly solutions described as "decomposed", which are at a temperature in the vicinity of 50°C, and although this temperature is less favourable than a higher one it is nevertheless sufficient to give satisfactory extraction yields. Moreover the stage where the solvent is regenerated and the gallium recovered is carried out in such a way that the organic phase is treated with an acid solution to recover the gallium at a temperature below that of the extraction stage and preferably near ambient temperature.

The very basic solutions treated by the methods described in these applications are particularly ones in which the $OH^-$ concentration may go up to 13—14 gram-ions/l. Thus the sodium aluminate lyes from the Bayer process usually have a composition corresponding to :

| | | |
|---|---|---|
| $Na_2O$ | : | 100—400 g/l |
| $Al_2O_3$ | : | 40—150 g/l |

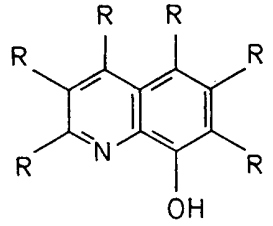
and the so-called "decomposed" lyes usually have a composition such as:

| | | |
|---|---|---|
| $Na_2O$ | : | 150—200 g/l |
| $Al_2O_3$ | : | 70—100 g/l |

Industrial installations used for this method are laid out as described in the said copending application.

A simpler industrial apparatus, which produces a less purified gallium, comprises a first counter-current extracting apparatus at the outlet of which, in a second such device operating in counter-flow, there is effected a single regeneration operation, by means of an acid solution, of the aluminium, sodium and gallium contained in the solvent.

It has been found that extended use of alkenyl-8-hydroxy-quinolines in a gallium extracting unit by the methods described in the said application leads to their gradual degradation, resulting in a reduction in their extracting power. In accordance with the present invention, the substituted hydroxyquinoline used in the process described and claimed in the specification of our copending application No. 29103/75 (1 513 398) has the general formula:

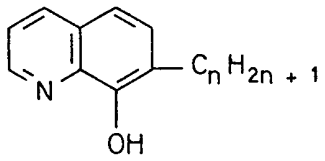


where each R is an alkyl radical or a hydrogen atom, the Rs being similar or dissimilar and at least one R being alkyl. It has been found that such compounds have a stability that does not deteriorate with prolonged use and that retains the remarkable properties of the alkenyl-8-hydroxyquinolines described in the said copending application, of extracting gallium from sodium aluminate lyes.

In a preferred embodiment of the invention the alkyl radical R has 5 to 20 carbon atoms. Below 5 carbon atoms, the substituted hydroxyquinolines according to the invention are generally found to be too soluble in an acid or basic medium, and the subsequent losses thus make it uneconomic to use them. Above 20 carbon atoms, the substituted hydroxyquinolines are too viscous to use easily.

In another embodiment of the invention the radical R is located in position 7 on the 8-hydroxyquinoline ring.

The preferred substances used in the method of the invention are of the general formula:




where *n* is preferably from 5 to 20.

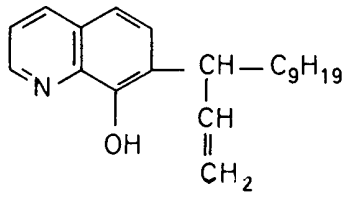
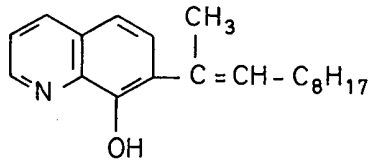
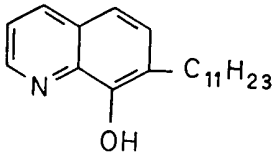
The hydroxyquinolines according to the invention make it possible to extract the gallium present in very basic aqueous solutions, particularly in sodium aluminate lyes from the Bayer process, almost totally without any loss in the course of time.

The following examples are given to illustrate the invention.

*Example 1*

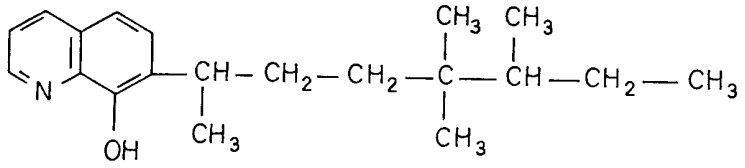
This example illustrates the degradation of alkenylhydroxyquinolines and the non-degradation of alkylhydroxyquinolines used in accordance with the invention under conditions of basicity equivalent to those of an aluminate lye from the Bayer process.

The hydroxyquinolines below are subjected to a rapid degradation test at 150°C in a 5M NaOH medium, the test being designed to classify the various products. The degradation rate is measured by chromatographic analysis of the resultant products in the gaseous phase after 24 and 72 hours.

| HYDROXYQUINOLINE TESTED | DEGRADATION RATE AFTER 24 HOURS | 72 HOURS |
|---|---|---|
| β alkenyl hydroxyquinoline  | 5% | 50% |
| α alkenyl hydroxyquinoline  | 100% | |
| alkylhydroxyquinoline  | No perceptible degradation | No perceptible degradation |

*Example 2*

This example illustrates the method of the invention when hydroxyquinoline A of the formula



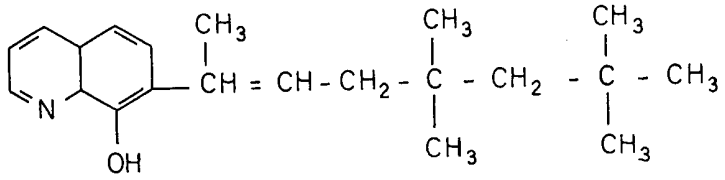
is used.

The gallium is extracted in an industrial extracting installation operating with continuous countercurrent flow, as described in the said copending application. A sodium aluminate solution composed of 90 g per litre $Al_2O_3$, 185 g/l $Na_2O$ and 250 mg/l Ga and an organic phase comprising an 8% solution of A in a 90—10 kerosene-decanol mixture is passed into a first countercurrent extracting apparatus. The extracting temperature is 50°C, the time of residence 1 hour and the ratio of the phases 1:1. In the second extracting apparatus the organic phase is put into contact with a regenerating solution comprising 6*N* hydrochloric acid. In the third extracting apparatus, operating at ambient temperature, the organic

phase is put into contact with a 1.8*N* hydrochloric acid solution. The gallium recovery rate is followed as a function of the time of operation of the installation. After 1000 hours of operation the gallium recovery rate is found to have maintained its initial value of 75%.

*Example 3*

This example is given as a comparison and illustrates the degradation of the gallium recovery rate in the course of time, when operating in the same illustration and under the same conditions as in Example 2, using hydroxyquinoline B of the formula:



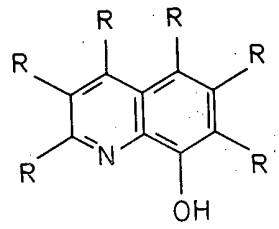
The results are as follows:

| Operating time | Gallium recovery rate |
|---|---|
| 1H | 76% |
| 10H | 48% |
| 40H | 34% |
| 280H | 20% |
| 760H | 18% |

Furthermore, although the effectiveness of regeneration by HCL is found to remain excellent and the recycled organic phase in all cases contains less than 5 mg/l of gallium before fresh contact with the Bayer lye, so that it is obviously possible to extract the gallium with product B, the use of product B is uneconomic because, if a suitable gallium extraction rate is to be maintained, more of product B has to be added in the course of extraction.

WHAT WE CLAIM IS:—

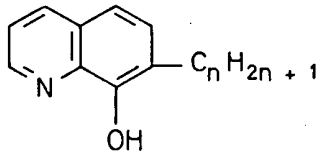
1. A method of recovering gallium present as a compound in solution in an aqueous alkaline solution having a pH of at least 14, comprising contacting the aqueous solution with an organic phase containing a water-immiscible substituted hydroxyquinoline of the general formula:



where each R, which is the same as or different from the others is a hydrogen atom or an alkyl group, subject to the proviso that at least one R is alkyl, separating the organic phase from the aqueous phase and then contacting the remaining organic phase with an aqueous acidic solution to remove gallium values from the organic phase to the aqueous phase, and then recovering the gallium values from the aqueous phase.

2. A method as claimed in Claim 1, in which R contains from 5 to 20 carbon atoms.

3. A method as claimed in Claim 1, in which the hydroxyquinoline has the general formula:




where $n$ is an integer.

4. A method as claimed in Claim 3, in which $5 \leqslant n \leqslant 20$.

5. A method as claimed in any one of the preceding claims, in which the very basic aqueous solutions treated by means of the organic phase are sodium aluminate solutions from units for producing alumina by the Bayer process and contain in particular gallium, aluminium and sodium.

6. A method as claimed in Claim 5, including the stages of putting the said sodium aluminate solution into contact with the said organic phase in such a way that the gallium and a certain quantity of sodium and aluminium pass from the aqueous phase to the organic phase; separating the organic phase from the aqueous phase; putting the organic phase into contact with a dilute aqueous solution of an acid to extract the sodium and aluminium from the organic phase, the gallium remaining in solution in the organic phase; separating the organic from the aqueous phase; putting the remaining organic phase into contact with a more concentrated aqueous acid solution to extract the gallium from the organic phase into the aqueous phase; and separating the gallium from the aqueous phase.

7. A method as claimed in Claim 6, in which the water-insoluble organic solvent is a halogenated or non-halogenated aliphatic or aromatic hydrocarbon.

8. A method as claimed in Claim 6 or 7, in which the acid used is hydrochloric, sulphuric or nitric acid.

9. A method as claimed in any one of Claims 6 to 8, in which the concentration of the dilute aqueous acid solution is from 0.4*N* to 0.8*N*.

10. A method as claimed in any one of Claims 6 to 9, in which the concentration of the more concentrated aqueous acid solution is over 1*N*.

11. A method as claimed in Claim 5, including the stages of putting the aqueous sodium aluminate solution from a unit producing alumina by the Bayer process into contact with the said organic phase, separating the organic from the aqueous phase; putting the organic phase into contact with a concentrated aqueous solution of an acid capable of chelating the gallium in anionic form, the gallium remaining in solution in the organic phase while the sodium and aluminium pass into the aqueous phase; separating the organic from the aqueous phase; putting the remaining organic phase into contact with a dilute aqueous acid solution to transfer the gallium from the organic to the aqueous phase; and separating the gallium from the aqueous phase.

12. A method as claimed in Claim 11, in which the water-insoluble organic solvent is a halogenated or non-halogenated aliphatic or aromatic hydrocarbon.

13. A method as claimed in Claim 11 or 12, in which the acid is hydrochloric acid or hydrobromic acid.

14. A method as claimed in any one of Claims 1 to 13, in which the concentrated aqueous acid solution has a concentration of from 5*N* to 8*N*.

15. A method as claimed in any one of Claims 11 to 14, in which the concentration of the dilute aqueous acid solution is from 1.3*N* to 2.2*N*.

16. A method as claimed in Claim 5, including the stages of putting the aqueous solution into contact with a water-insoluble substituted hydroxyquinoline in solution in a water-insoluble halogenated or non-halogenated aliphatic or aromatic hydrocarbon in such a way that the gallium and a certain quantity of sodium and aluminium transfer from the aqueous phase to the organic phase; separating the organic phase from the aqueous phase; putting the organic phase into contact with an aqueous solution of an acid to extract the sodium, aluminium and gallium from the organic phase; separating the aqueous and organic phases; and recovering the gallium, sodium and aluminium.

17. A method as claimed in Claim 16, in which the acid used in sulphuric acid or nitric acid in a concentration higher than 1.6*N*, or hydrochloric or hydrobromic acid in a concentration of from 1.3*N* to 2.2*N*.

18. A method as claimed in any one of Claims 6 to 17, in which the aqueous sodium aluminate solution is put into contact with the organic phase at an elevated temperature.

19. A method as claimed in Claim 18, in which the said temperature does not exceed 100°C.

20. A method as claimed in any one of Claims 6 to 17, in which the organic phase charged with gallium is treated with an aqueous acid solution to recover the gallium at a temperature below that at which the aluminate solution is put into contact with the organic phase.

21. A method as claimed in Claim 20, in which the temperature used is ambient temperature.

22. A method as claimed in Claim 1, substantially as hereinbefore described in Example 1 or 2.

23. Gallium, when recovered by a method as claimed in any one of the preceding claims.

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