



PATENT SPECIFICATION

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DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process of Separation of Components from a Mixture by Liquid-Liquid Extraction

We, THORIUM LIMITED whose registered office is at 9 Basinghall Street, E.C.2., in the City of London, England, formerly of Barrington House, Gresham Street, London, E.C. 2, a Company registered under the Laws of Great Britain, 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 separation of components from a mixture, and relates more especially to the separation of components from a mixture by liquid-liquid extraction.

If two solutes (*a* and *b*) are dissolved in a first solvent phase S1 which is then contacted with a second solvent phase S2 in which solute *a* is insoluble, clearly the solute *b* will be transferred to, and be present in, the second phase S2 in a pure form. By an extension of this reasoning, it can be seen that if solute *a* instead of being insoluble in the solvent phase S2 is merely less soluble than solute *b*, an enrichment of the second solvent phase S2 with solute *b* is to be expected, although purification will not take place in one stage as before.

In the case therefore where both solutes are soluble, albeit to different extents, in the solvent phase S2 further separation is often needed to get a ~~value~~ concentration or a purification of one solute with respect to the other. This further separation can be achieved by contacting the first solvent phase S1 now depleted with respect to solute *b* with a fresh portion of second solvent phase S2 or by contacting the used second solvent phase S2 enriched with respect to solute *b* with a fresh portion of first solvent phase S1 containing both solutes *a* and *b*.

This can obviously be elaborated into the conventional liquid-liquid extraction installation, comprising a plurality of linked con-

tacting and settling stages through which two solvent phases pass countercurrently so that one of two solutes is preferentially extracted from one solvent phase.

Moreover, this type of installation is of general utility where it is required to separate two transferable agents by means of two streams of transferring agent moving countercurrently.

In the above form, however, such a method is suitable only for continuous separation or continuous concentration of the transferable agents. The present invention relates to a modification of the above method which enables a batch separation to be carried out, and is based on the phenomenon of "reflux" in such a countercurrent separation installation. This is best explained by analogy.

The reflux ratio in a fractional distillation is a measure of the extent to which a product is removed from the head of a distillation column compared to the extent to which that product recondenses and falls back into the vessel being heated. Thus, "total reflux" implies that product is not taken off, but is all allowed to fall back. Eventually such a system comes to equilibrium.

Similarly, the reflux ratio in a liquid-liquid extraction installation is a measure of the extent to which solute is removed from one end. If solute is not removed from the end unit of such an installation (or if all the solute is recycled to this end unit, which comes to the same thing) total reflux will occur and equilibrium will eventually be attained.

The invention consists in a batch method of separating two or more solutes by means of two immiscible or partially-miscible solvents flowing in countercurrent, in which a total reflux condition is achieved by returning all solutes leaving either end of the apparatus in either solvent stream to the same end from which they have come until an equilibrium condition has been achieved, when

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[Price 4s. 6d.]



the process is stopped and the solvent fractions in which the desired solutes have become concentrated are removed.

5 The method of the invention is especially applicable to the separation of two or more solutes, e.g. rare earth salts such as nitrates, by means of two solvent phases, e.g. tributyl phosphate and water, flowing countercurrently.

10 Any method of obtaining total reflux may be used. Thus, it may be attained by scrubbing one outgoing solvent phase to remove completely the solutes contained therein and returning the solutes obtained to the end of the installation whence they came for further separation. Scrubbing is preferably carried out using a relatively large flow of the other solvent phase, which is then concentrated before being returned for further separation.

20 Alternatively, total reflux may be attained by concentrating one outgoing solvent phase at a rate of loss of bulk equivalent to its rate of flow and returning it to that end of the separating installation whence it came. It may, in fact, be evaporated to dryness and the solute thus obtained taken up in the other ingoing solvent phase.

25 Of course, one method of obtaining total reflux may be used at one end, and another at the other end, of the installation; moreover, as a preferred feature, one or both solvents may be recycled.

30 The invention further consists in a batch method of separating soluble rare earth salts using countercurrent streams of tributyl phosphate and water, which is operated using total reflux at each end of a liquid-liquid countercurrent extraction installation, and in which total reflux is obtained at one end by scrubbing the outgoing solvent phase with the ingoing solvent phase and at the end by concentrating the outgoing solvent phase and recycling it, the system being allowed to come to equilibrium and extraction stages of suitable composition being then removed.

35 In general, total reflux may be obtained by chemical methods. For instance, rare earth nitrates as used in the method of the preceding paragraph may be precipitated from the outgoing solvent stream as carbonates or hydroxides, and the precipitates may be dissolved up again in acid for recycling.

40 It is an especial feature of the invention that the contents of extraction stages may be removed from intermediate stages as well as end stages, since concentration peaks of the various components are set up. To help in the efficiency of separation, certain stages of the liquid-liquid extraction installation may be enlarged, since for economical production rates, the ratio of weight of material unloaded from selected units to the weight of material left behind as an incompletely separated mixture must not be too small.

45 The size or the quantity of units which will

contain the desired products will be determined by the proportion of solutes initially present.

50 An interesting feature of the total reflux condition is that separation achieved per unit is a maximum. The equilibrium state reached under total reflux is defined by the following equation.

$$\frac{A_1}{B_1} = \beta \frac{A_n}{B_n}$$

70 where A and B are two components being separated. $\frac{A_1}{B_1}$ is the ratio of these components in one of the solvent phases in the

1st mixer settler and $\frac{A_n}{B_n}$ is the ratio in the same solvent phase in the nth mixer settler. β is the separation factor and is the ratio of the partition coefficients of A and B between the two solvents.

80 This simple relationship permits the calculation of the number of units required to separate the components adequately at equilibrium.

85 Under total reflux conditions, products are not continuously withdrawn from the system and the flow of material in the one solvent is balanced by the flow of material in the other solvent in the opposite direction. Instead of continuous production of separated component, the components to be separated are dissolved in each of the two solvents at the preferred concentration and these solvent solutions are initially added to the units in a suitable ratio. The installation is then operated under total reflux until the required separation is obtained.

90 The products of the process consist of material obtained by emptying only those units which have reached a predetermined purity, the positions of the units in question being indicated by the above formula. These units may then be refilled with the mixture and the installation again operated under total reflux.

95 For example, if three components are being separated and a sufficient number of units is used concentrates of the components can be withdrawn from the two ends and from some of the middle units.

100 The invention will be further described with reference to the accompanying drawings, in which:

105 Figure 1 shows in diagrammatic form a separating installation according to the invention in the form of a liquid-liquid countercurrent extraction installation.

110 Figures 2 and 3 show one end of the

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Unit
Pr/N
ratio

installation with alternative means of bringing about reflux.

The liquid-liquid separating installation of Figure 1 comprises a separating region 1, consisting of a plurality of mixer-settler countercurrent stages as known *per se*, a scrubbing region 2 consisting of similar mixer-settler stages, and two evaporators 3 and 4.

When this installation is in operation, two solvent phases S1 and S2 flow in countercurrent through the installation. S1 scrubs the outgoing S2 free from solutes and is then decreased in bulk in evaporator 3 to a predetermined solute concentration. This concentrated S1 is then passed in countercurrent with S2 through the separating region 1, wherein the two solutes are distributed towards one end or the other of the separating region. The S1 phase emerging is again decreased in bulk in evaporator 4, and then recycled into the S1-out end of the separating region 1. It will be clear that the two decreases in bulk should be equivalent to the amount of S1 used, so that there is no net flow of solvent out of the installation. It is obviously convenient for S2 to be recycled, since it enters and leaves the installation in pure form; moreover, if necessary S1 can be condensed and recycled from the two evaporators. These two recycling steps are however not strictly necessary to the method according to the invention.

The scrubbing region 2 with its associated evaporator 3, and the evaporator 4, perform equivalent functions. Thus, the method according to the invention could equally well be carried out with a scrubbing region plus evaporator at each end, or with an evaporator alone at each end or some other combination. Figure 2, for example, shows a scrubbing region 5 at the S2-in end scrubbing the S1-out completely, S2 being concentrated at 6 before being fed back as S-2 feed to the separating region 1. Figure 3 shows an alternative form of evaporator which can be used for the function of evaporator alone. In this, the solutes are evaporated to dryness and taken up in the S-2 feed, as shown by chain-dotted lines.

Although the above description has taken the case of two solutes in detail, the method of the present invention is not limited to such a case and is in fact especially useful for separations involving more than two solutes as shown in the examples.

The invention will be still further described with reference to the following Examples

which illustrate methods of separating rare earth nitrates using countercurrent streams of tributyl phosphate (TBP) and water. However, these Examples are only given by way of illustration, and the method of the invention can be used to separate the members of any group of related chemical compounds which have different solubilities in two different solvents.

EXAMPLE 1:

The method of operation of the process is best described with reference to Figure 1 of the accompanying drawings, in which S2 is the TBP and S1 is the aqueous stream.

Praseodymium and neodymium nitrates were dissolved in TBP to give a concentration of rare earths of 190 g./l of rare earths expressed as oxides. A similar aqueous solution but containing 460 g./l was also made up, and these two solutions were placed in the mixer-settlers of the separating region 1 (in this case 12 stages were used) and made to flow in countercurrent, further aqueous solution of 460 g./l concentration being fed in at the aqueous-in end at 4.6 ml./min.; and pure TBP at the aqueous-out end at 10 ml./min.

The TBP leaving at the aqueous-in end contains rare earth nitrates and is accordingly scrubbed in scrubbing region 2 (which in this case has five stages) with a relatively large amount of pure water (20 ml./min.) so that all the rare earth nitrates are removed and total reflux is obtained. The relatively weak aqueous solution is concentrated to 460 g./l and fed into the aqueous-in end of the separating region 1 at 4.6 ml./min. as the aqueous feed while the scrubbed TBP is recycled.

At the aqueous-out end, the aqueous solution is again concentrated to 460 g./l and fed back to the aqueous-out end at 10 ml./min. This brings about total reflux at this end, since, as it will be observed from Figure 2, evaporation to 460 g./l at each end ensures that the 20 ml./min. of water entering is all evaporated.

The time required for one volume charge was given by the total volume of both solvents in the 12 mixer-settler stages divided by the combined rate of 14.6 ml./min. The process was continued for sufficient time to give four volume changes.

Analysis of the aqueous phases in the 12-stage section gave the following results:

Unit No. Pr/Nd ratio	1	2	3	4	5	6	7	8	9	10	11	12
	4.8	4.1	3.0	2.0	1.5	1.2	.8	.6	.4	.29	.21	.16

The end stages were then removed and treated to recover the rare earths.

EXAMPLE 2:

Separation of a praseodymium concentrate

from lanthanum, neodymium and yttrium and other rare earths was achieved in a similar experiment using 21 units. Analysis after 5 volume changes showed the following results:—

Analysis of Units

Unit No.	%Pr ₆ O ₁₁	%Nd ₂ O ₃	% Rest	
1	0.7	—	99.3	(Mainly La ₂ O ₃)
3	2.6	—	97.3	
5	10.2	0.17	89.6	
7	35.5	0.8	59.6	
9	67.5	2.1	30.4	
11	86.4	3.8	9.8	(Mainly Y and other earths)
13	88.2	6.5	5.3	
15	81.7	11.3	7.0	
17	66.0	16.8	17.2	
19	43.7	17.7	38.6	
21	21.6	12.9	65.5	

*Any La, Y and other earths included in this figure.

10 It will be observed from the above Example that a useful concentrate can collect in intermediate stages of the installation and simultaneous separations of Pr, La, Nd, Y and other earths achieved.

15 Thus, the invention is not limited to separating two components, but when equilibrium is set up there may be a peak concentration of a component in some intermediate stage of the separator.

EXAMPLE 3:

A similar experiment was carried out using 50 stages of mixer-settlers. A mixture of rare earths was separated consisting mainly of lanthanum, praseodymium, neodymium, samarium, yttrium and small amount of the heavy earths.

After four volume changes the mixer-settler units were analysed and gave the following results for certain units containing suitable concentrate:—

Mixer-settler No.	%Pr ₆ O ₁₁	%Nd ₂ O ₃	% Other R.E. oxides
1 - 19 inclusive	0.01	—	ca. 100% ha ₂ O ₃
28	57.6	1.0	41.4
29	80.2	1.9	17.9
30	89.5	3.0	7.5
31	92.7	4.9	2.4
32	91.3	6.8	1.9
33	88.7	10.6	0.7
45	10.4	89.1	0.5
46	8.6	91.1	0.3
47	6.1	91.5	2.4
48	4.6	90.1	5.3
49	3.6	88.2	8.2
50	2.6	79.8	17.6

(N.B.) Other rare earths in Nos. 28 - 33 mainly La₂O₃; on Nos. 45 - 50, other rare earths Sm₂O₃, Y₂O₃ and heavies).

Useful lanthanum, praseodymium, and neodymium products were thus obtained in the one experiment.

WHAT WE CLAIM IS:—

1. A batch method of separating two or more solutes by means of two immiscible or partially-miscible solvents flowing in counter-

The end stages were then removed and treated to recover the rare earths.

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Analysis of Units

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1	0.7	—	99.3	(Mainly La ₂ O ₃)
3	2.6	—	97.3	
5	10.2	0.17	89.6	
7	35.5	0.8	59.6	
9	67.5	2.1	30.4	
11	86.4	3.8	9.8	(Mainly Y and other earths)
13	88.2	6.5	5.3	
15	81.7	11.3	7.0	
17	66.0	16.8	17.2	
19	43.7	17.7	38.6	
21	21.6	12.9	65.5	

*Any La, Y and other earths included in this figure.

10 It will be observed from the above Example that a useful concentrate can collect in intermediate stages of the installation and simultaneous separations of Pr, La, Nd, Y and other earths achieved.

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Mixer-settler No.	%Pr ₆ O ₁₁	%Nd ₂ O ₃	% Other R.E. oxides
1 - 19 inclusive	0.01	—	ca. 100% ha ₂ O ₃
28	57.6	1.0	41.4
29	80.2	1.9	17.9
30	89.5	3.0	7.5
31	92.7	4.9	2.4
32	91.3	6.8	1.9
33	88.7	10.6	0.7
45	10.4	89.1	0.5
46	8.6	91.1	0.3
47	6.1	91.5	2.4
48	4.6	90.1	5.3
49	3.6	88.2	8.2
50	2.6	79.8	17.6

(N.B.) Other rare earths in Nos. 28 - 33 mainly La₂O₃; on Nos. 45 - 50, other rare earths Sm₂O₃, Y₂O₃ and heavies).

Useful lanthanum, praseodymium, and neodymium products were thus obtained in the one experiment.

WHAT WE CLAIM IS:—

1. A batch method of separating two or more solutes by means of two immiscible or partially-miscible solvents flowing in counter-

current, achieved end of i to the s until a achieved solvent have be 2. A applied soluble r 3. A which th separatec 15 flowing i 4. A ceding cl by scrub remove 20 therein a the end c further se 5. A which sci 25 tively lar which is for furthe 6. A n claims 1 t 30 by concer at a rate rate of fl of the sep 7. A n claims 1 t 35 phase is e thus obtai solvent ph 8. A m claims 1 t 40 used to se



current, in which a total reflux condition is achieved by returning all solutes leaving either end of the apparatus in either solvent stream to the same end from which they have come until an equilibrium condition has been achieved, when the process is stopped and the solvent fractions in which the desired solutes have become concentrated are removed.

2. A method as claimed in claim 1 when applied to the separating of mixtures of soluble rare earth salts.

3. A method as claimed in claim 2 in which the rare earth salts are nitrates and are separated using tributyl phosphate and water flowing in countercurrent.

4. A method as claimed in any one preceding claim in which total reflux is attained by scrubbing one outgoing solvent phase to remove completely the solutes contained therein and returning the solute obtained to the end of the installation whence it came for further separation.

5. A method as claimed in claim 4 in which scrubbing is carried out using a relatively large flow of the other solvent phase, which is concentrated before being returned for further separation.

6. A method as claimed in any one of claims 1 to 3 in which total reflux is attained by concentrating one outgoing solvent phase at a rate of loss of bulk equivalent to its rate of flow, and returning it to that end of the separating installation whence it came.

7. A method as claimed in any one of claims 1 to 3 in which one outgoing solvent phase is evaporated to dryness and the solute thus obtained taken up in the other ingoing solvent phase.

8. A method as claimed in any one of claims 1 to 3 in which chemical methods are used to separate the solutes from one solvent

stream and these separated solutes are subsequently transferred to the other solvent stream in order to bring about total reflux.

9. A method as claimed in claim 8 as dependent on claim 3 in which the rare earth nitrates in the outgoing solvent stream are precipitated as hydroxide or carbonates and the precipitate dissolved up again in acid for recycling.

10. A method as claimed in claim 8 (as dependent on claim 2) in which a more extractable component is added to the aqueous-in end of the installation to displace the less extractable rare earths.

11. A method as claimed in claim 9 in which nitric acid is added to the aqueous-in end of the installation as the more extractable component to displace the less extractable rare earths.

12. A method as claimed in any one of claims 4 to 11 in which pure solvent phase obtained by total reflux is recycled to the other end of the apparatus than that to which the solute removed from the said solvent is returned.

13. A method as claimed in any one of the preceding claims when carried out in a liquid-liquid extraction installation a proportion of the stages of which are enlarged.

14. A batch method of separating two or more solutes by means of two immiscible or partially miscible solvents, substantially as hereinbefore particularly described with reference to, and as illustrated in, the accompanying drawings.

15. A concentrate obtained by the method as claimed in any one of the preceding claims.

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