

COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

I  
We

Rohm and Haas Company,  
Independence Mall West,  
Philadelphia,  
Pennsylvania 19105,  
UNITED STATES OF AMERICA.

596133

hereby apply for the grant of a Standard Patent for an invention entitled:

ION EXCHANGE RESIN MIXTURES AND THEIR  
USE IN CATION EXCHANGE PROCESSES

which is described in the accompanying ~~document~~ complete specification.

Details of basic application(s):—

<u>Number</u>	<u>Convention Country</u>	<u>Date</u>
8530275	United Kingdom	9th December 1985.

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED ..... 14. 2. 90 .....

The address for service is care of DAVIES & COLLISON Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 4th day of December 19 86.

*H. V. Pinnington*

To: THE COMMISSIONER OF PATENTS

.....  
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

Insert title of invention.

In support of the Application made for a patent for an invention entitled: "ION EXCHANGE RESIN MIXTURES AND THEIR USE IN CATION EXCHANGE PROCESSES"

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I am KENNETH NORMAN RIMINGTON, Patent Attorney, of Davies & Collison, 1 Little Collins Street, Melbourne 3000, Victoria, Australia

do solemnly and sincerely declare as follows :-

- 1. (a) I am the applicant for the patent. We are or (b) I am authorized by ROHM AND HAAS COMPANY

the applicant..... for the patent to make this declaration on its behalf.

- 2. (a) I am the actual inventor of the invention. We are or (b) Alain Denis Louis PRUNAC, of 92 Rue de Cornouailles, 78180 Montigny-Le-Bretonneux, France; Daniel Michel BAUR, of Le Solimar A.1, Chemin Des Combes, 06600 Antibes, France; Jean Pierre Marcel POIRSON, of Clos De Mougins, 107/2 Impasse Des Chenes, 06250 Mougins, France

the actual inventor..... of the invention and the facts upon which the applicant..... is entitled to make the application are as follows :-

The applicant would, if a patent were granted on an application made by the said inventors, be entitled to have the patent assigned to it.

3. The basic application..... as defined by Section 141 of the Act was made in United Kingdom on the 9th December, 1985 by Rohm and Haas Company in ..... on the ..... by ..... on the ..... in ..... on the ..... by .....

4. The basic application..... referred to in paragraph 3 of this Declaration was the first application..... made in a Convention country in respect of the invention the subject of the application.

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

Insert place and date of signature.

Declared at Melbourne this 23rd day of January, 1987.

Signature of declarant(s) (no attestation required)

Handwritten signature of K. N. Rimington

Note: Initial all alterations.



(11) AU-B-66086/86  
(10) 596133

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8. A process for treating a liquid according to any preceding claim, wherein the level of organic material leached from the resin mixture into the treated liquid is maintained at not more than 3 mg/l of liquid.

9. A process for treating a liquid according to any preceding claim, which also comprises, as bio-filter, ion exchange resin which has been impregnated with silver.

COMMONWEALTH OF AUSTRALIA

PATENT ACT 1952

COMPLETE SPECIFICATION

(Original)

FOR OFFICE USE

Class Int. Class

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Lodged:

66 086/86

Complete Specification Lodged:  
Accepted:  
Published:

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Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant:

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UNITED STATES OF AMERICA.

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DAVIES & COLLISON, Patent Attorneys,  
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Complete Specification for the invention entitled:

ION EXCHANGE RESIN MIXTURES AND  
THEIR USE IN CATION EXCHANGE PROCESSES

The following statement is a full description of this invention,  
including the best method of performing it known to us :-

ION EXCHANGE RESIN MIXTURES AND THEIR USE IN CATION  
EXCHANGE PROCESSES

The present invention is concerned with ion  
exchange resin mixtures and their use in cation  
5 exchange processes, such as food processing and/or  
potable water production so that organic material  
leached from the resin mixture during such processes is  
maintained at an acceptable level in the treated  
liquid. For example, these resin mixtures enable the  
10 production of softened water having a level of leached  
organic material which is low enough for the water to  
be acceptable for potable water applications. By "food  
processing" we mean cation exchange processes used in  
the treatment of liquids for use in the production or  
15 processing of materials for human consumption.

It is known to soften water, i.e. to remove  
primarily calcium and magnesium hardness ions from the  
water, by passing the water through cation exchange  
resin but this procedure is not always acceptable for  
20 the production of potable water as organic material can  
leach from the resin into the water during treatment  
and result in too high a level of leached organic  
material in the softened water for potability. At  
present, the recommendation in some countries is that  
25 resin will be acceptable for the production of potable  
water if the level of organic material leaching from  
the resin is not more than 3 mg/litre of water,  
expressed as total organic carbon and measured by the  
procedure of DIN Standard 54411.

30 It is, therefore, clearly desirable, during  
softening of water with cation exchange resin, to  
maintain a level of this leached organic material such  
that the softened water is potable.

It is known to deionize water by passing it sequentially through cation exchange resin and then anion exchange resin, the volume ratio of anion exchange resin to cation exchange resin usually being  
5 of the order of 1:1. During such deionization it has been observed that organic material leaching into the water from the cation exchange resin is absorbed by the anion exchange resin and it might be expected that effective absorption of leached organic material will  
10 also occur using somewhat less anion exchange resin in a sequential treatment.

What we have now surprisingly found is that softened water having a leached organic material level low enough for potability can be produced by passing  
15 the water through a resin mixture comprising (a) cation exchange resin and (b) only 0.5 to 20% by volume, of (a) plus (b), of anion exchange resin. The effectiveness of such a resin mixture is surprising in view of the lower degree of contact of any leached  
20 organic material with such a low amount of anion exchange resin dispersed throughout the cation exchange resin as opposed to a similar amount in a sequential treatment. The use of a single resin bed, of course, has the inherent advantages over the use of separate  
25 beds, for example, simplification of transportation and storage of resin, simplification of the equipment required for the softening process, and the economic advantages associated therewith.

~~According to the present invention there is~~  
30 provided an ion exchange resin mixture, which comprises:-

- (a) cation exchange resin; and
- (b) acrylic and/or styrenic anion exchange resin;



1 According to the present invention there is provided a  
2 process for treating a liquid, e.g. water, to remove cations  
3 therefrom, comprising passing the liquid to be treated  
4 through a bed of ion exchange resin, characterised in that  
5 the resin comprises a mixture of:-

- 6 (a) cation exchange resin; and
  - 7 (b) acrylic and/or styrenic anion exchange resin;
- 8 resin (b) being present in an amount of 0.5% to 20% by  
9 volume, based on the total volume of (a) plus (b), and the  
10 level of organic material leached from the resin mixture  
11 into the treated liquid is maintained at an acceptable  
12 level.

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~~wherein (b) is present in an amount of 0.5% to 20% by volume, based on the total volume of (a) and (b).~~

The present invention also provides a <sup>preferred</sup> process for treating a liquid to remove cations, for example  
5 hardness ions, therefrom, the process comprising passing the liquid to be treated through a bed of the resin mixture of the invention so that the level of organic material leached from the resin mixture into  
10 the treated liquid is maintained at an acceptable level, for example, by using a resin mixture having a leachable organic material level, expressed as total organic carbon and measured by the procedure of DIN Standard 54411, of not more than 3 mg/litre of liquid.

15 Examples of suitable applications of the process of the present invention are in the treatment of water to produce softened, potable water, and in sugar processing, for example, to remove hardness ions or monovalent cations from sugar syrup.

20 Resin (a) may comprise strongly and/or weakly acidic cation exchange resin. Further, resin (a) may comprise gel-type and/or macroreticular (otherwise known as macroporous)-type acidic cation exchange resin. The exchangeable cations of strongly acidic cation exchange resins are preferably alkali and/or  
25 alkaline earth metal cations, and the exchangeable cations of weakly acidic cation exchange resins are preferably H<sup>+</sup> and/or alkali metal cations.

30 Suitable strongly acidic cation exchange resins include styrene/divinyl benzene cation exchange resins, for example, styrene/divinyl benzene resins having sulfonic functionality and being in the Na<sup>+</sup> form such as Amberlite 200, Amberlite 252 and Duolite C26, which are macroreticular-type resins, and Amberlite IR-120, Amberlite IR-122, Amberlite IR-132, Duolite C20 and



Duolite C206, which are gel-type resins. Suitable weakly acidic cation exchange resins include acrylic cation exchange resins, for example, Amberlite XE-501, which is a macroreticular-type acrylic cation exchange resin having carboxylic functionality and being in the  $H^+$  form, and Amberlite DPl which is a macroreticular-type methacrylic/divinyl benzene resin having carboxylic functionality and being in the  $Na^+$  form.

Resin (b) may comprise strongly and/or weakly basic anion exchange resin. Further, resin (b) may comprise gel-type and/or macroreticular-type basic anion exchange resin. If resin (b) comprises styrenic anion exchange resin, then such styrenic resin is preferably macroreticular. Preferably, the exchangeable anions of resin (b) are chloride and/or sulfate ions. Suitable strong base anion exchange resins include those having quaternary ammonium functionality such as the following all of which are in the chloride form: Amberlite IRA-458, which is a gel-type acrylic resin having trimethyl ammonium functionality; Amberlite IRA-900 which is a macroreticular-type styrene/divinylbenzene resin having trimethylammonium functionality; Amberlite IRA-400, which is a gel-type styrene/divinylbenzene resin having trimethyl ammonium functionality; and Duolite ES-196 which is a macroreticular styrene/divinylbenzene resin having triethylammonium functionality. Suitable weak base anion exchange resins include Amberlite IRA-93 which is a macroreticular styrene/divinylbenzene resin in the free base form.

Before use of the anion exchange resin in accordance with the present invention it may be cleaned, for example by washing it with hot water, to remove any organic material that is present and that

may otherwise leach out of it during such use.

5 The lower limit for the amount of resin (b) in the resin mixture of the invention is preferably 2%, more preferably 3% and most preferably 4%, by volume, based on the total volume of resins (a) plus (b). The upper limit for the amount of resin (b) in the resin mixture of the invention is preferably 15%, more preferably 10% and most preferably 6%, by volume, based on the total volume of resins (a) plus (b).

10 The resin mixture of the invention may, for example, additionally comprise, as bio-filter, ion exchange resin which has been impregnated or coated with silver. The bio-filter resin may, for example, comprise silver-containing strongly basic anion exchange resin and/or silver-containing strongly acidic cation exchange resin. Suitable silver-containing strongly basic anion exchange resins include styrene/divinyl benzene resins, for example, silver-containing macroreticular-type styrene/divinyl benzene resins which have trimethyl ammonium functionality and are in the chloride form such as Ambergard XE 342. Suitable silver-containing strongly acidic cation exchange resins include Duolite C 26 AG which is a silver-containing macroreticular styrene/divinylbenzene resin having sulfonic functionality and in the  $\text{Na}^+$  form.

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35 The process according to the present invention enables the production of treated liquid, for example, softened water, having a level of organic material which is considerably lower than that achieved by the use of a strongly acidic cation exchange resin alone, this lower level of organic material being achieved by the take-up, by the acrylic and/or styrenic anion exchange resin, of organic material that may leach into the liquid from the acidic cation exchange resin.

The present invention will now be further illustrated by way of the following Examples which are for illustrative purposes only and are not to be construed as imposing any limitation on the scope of the invention.

EXAMPLE 1:-

400 ml of a 95% by volume Amberlite IR-120 and 5% by volume Amberlite IRA-458 resin mixture were placed in a 40 millimetre internal diameter glass column and rinsed upwardly over a period of 2 hours with two litres of deionized water.

The resin-containing column was then connected, via a pump, to a glass reservoir containing 4 litres of deionized water having an initial Total Organic Carbon content (TOC), as measured by a commercial TOC analyser, of 0.4 mg/l of water. The water from the reservoir was then percolated downwardly through the resin mixture at a flow rate of 5.7 l/hour and returned to the reservoir (this procedure being continued for a period of 7 days).

At the end of this procedure, the TOC of the water in the reservoir had increased by only 2.5 mg/l of water, which is below the maximum amount of leached organic material tolerated, under the present West German Regulations, for food processing and potable water utilization.

The above test procedure corresponds to the BGA Recommendation XXIV, and the complete testing procedure and equipment are those of the DIN Standard 54411.

COMPARATIVE EXAMPLE A:-

Example 1 was repeated except that Amberlite IR-120 was used alone in the column.

5 After percolation of the water through the resin-containing column for a period of 7 days, it was found that the TOC of the water had increased by 3.5 mg/l, 3 mg/l being the presently recommended maximum limit under the present West German regulations.

EXAMPLE 2:-

10 Example 1 was repeated except that the Amberlite IR-120 was replaced by Amberlite XE-501. In this Example the increase in the TOC of the water, after percolation through the resin mixture for 7 days, was observed to be 1.3 mg/l of water.

15 COMPARATIVE EXAMPLE B:-

Example 2 was repeated except that Amberlite XE-501 was used alone in the column. After percolation of the water through the resin for 7 days, it was observed that the TOC of the water had increased by 20 6 mg/l of water when compared with the initial TOC of the water.

Example 3:-

25 Example 1 was repeated except that the Amberlite IRA-458 in the resin mixture was replaced with Amberlite IRA-93 which is a weakly basic macroreticular styrenic anion exchange resin.

30 After percolation of the water through the resin-containing column for a period of 7 days, it was found that the TOC of the water had increased by only 1.1 mg/l of water.

Example 4:-

Example 1 was repeated except that the Amberlite IRA-458 was replaced with Amberlite IRA-400 which is a strongly basic gel-type styrenic anion exchange resin.

5 After percolation of the water through the resin-containing column for a period of 7 days, it was found that the TOC of the water had increased by only 2.4 mg/l of water.

Example 5:-

10 Example 4 was repeated except that a 98% by volume Amberlite IR-120 and 2% by volume Amberlite IRA-400 resin mixture was used.

After percolation of the water through the resin-containing column for a period of 7 days, it was found that the TOC of the water had increased by 3.3 mg/l of water, which, although being a greater increase in TOC than when the resin mixture contained 5% by volume Amberlite IRA-400 (Example 4), is still lower than the increase in TOC achieved when Amberlite IR-120 is used alone (Comparative Example A).

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Example 6:-

Example 1 was repeated except that the Amberlite IR-120 was replaced by Amberlite IR-252.

After percolation of the water through the resin-containing column for a period of 7 days, it was found that the TOC of the water had increased by only 0.8 mg/l of water.

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Example 7:-

Example 6 was repeated except that the Amberlite IRA-458 was replaced by Amberlite IRA-900.

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After percolation of the water through the resin-containing column for 7 days, it was found that the TOC of the water had increased by only 1.5 mg/l of water.

5 Example 8:-

An ion exchange resin mixture of 14.3 litres of Amberlite IR-120 and 0.7 litres of Amberlite IRA-458 was placed in the ion exchange resin container of a standard water softening apparatus for domestic usage. 10 Water having a total hardness of 378 mg/l, as calcium carbonate, was fed to the softener at a flow rate of 225 litre per hour and after 30 minutes of operation the TOC and total hardness (as calcium carbonate) in the treated water at the outlet of the softener were 0.4 mg/l and less than 1 mg/l, respectively. 15 After 60 minutes of operation the TOC and total hardness (as calcium carbonate) at the outlet of the softener were less than 0.1 mg/l and less than 1 mg/l, respectively.

COMPARATIVE EXAMPLE C:-

20 Example 8 was repeated except that 15 litres of Amberlite IR 120 was used alone in the ion exchange resin container of the softener.

After 30 minutes of operation the TOC and total hardness (as calcium carbonate) of the water at the outlet of the softener were 1.6 mg/l and less than 1 mg/l, respectively, and after 60 minutes of operation 25 the TOC and total hardness (as calcium carbonate) of the water at the outlet of the softener were 0.9 mg/l and less than 1 mg/l, respectively.

30 The above Examples show the effectiveness of the anion exchange resin in (i) maintaining the leached

organic material level of the cation exchange resin acceptably low both when treated using the procedure of DIN Standard 54411 (see Examples 1 to 4, 6 and 7 and Comparative Examples A and B) and under actual use conditions (see Example 8 and Comparative Example C), (ii) maintaining the level of leached organic material lower than when cation exchange resin is used alone (see Examples 1 to 8 and Comparative Examples A, B and C).

"Amberlite" and "Ambergard" are Trade Marks of Rohm and Haas Company, and "Duolite" is a Trade Mark of Duolite International S.A.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for treating a liquid, e.g. water, to remove cations therefrom, comprising passing the liquid to be treated through a bed of ion exchange resin, characterised in that the resin comprises a mixture of:-

(a) cation exchange resin; and

(b) acrylic and/or styrenic anion exchange resin; resin (b) being present in an amount of 0.5% to 20% by volume, based on the total volume of (a) plus (b), and the level of organic material leached from the resin mixture into the treated liquid is maintained at an acceptable level.

2. A process for treating a liquid according to claim 1, wherein resin (b) is present in an amount of 0.5 to 15% by volume, based on the total volume of (a) plus (b).

3. A process for treating a liquid according to claim 2, wherein resin (b) is present in an amount of 3 to 10%, especially 4 to 6%, by volume, based on the total volume of (a) plus (b).

4. A process for treating a liquid according to any preceding claim, wherein resin (a) comprises strongly acidic cation exchange resin in which the exchangeable cations are alkali metal and/or alkaline earth metal cations, and/or weakly acidic cation exchange resin in which the exchangeable cations are H<sup>+</sup> and/or alkali metal cations.

5. A process for treating a liquid according to claim 4, wherein the strongly acidic cation exchange resin comprises styrene/divinylbenzene resin having sulfonic functionality and being in the Na<sup>+</sup> form.

6. A process for treating a liquid according to claim 4, wherein the weakly acidic cation exchange resin comprises acrylic cation exchange resin having carboxyl functionality and being in the H<sup>+</sup> or Na<sup>+</sup> form.

7. A process for treating a liquid according to any preceding claim, wherein (b) comprises strong base anion exchange resin having quaternary ammonium functionality and being in the chloride form.

8. A process for treating a liquid according to any preceding claim, wherein the level of organic material leached from the resin mixture into the treated liquid is maintained at not more than 3 mg/l of liquid.

9. A process for treating a liquid according to any preceding claim, which also comprises, as bio-filter, ion exchange resin which has been impregnated with silver.

10. Use of a bed of ion exchange resin for treating potable water to remove cations from the water, wherein the ion exchange resin comprises a mixture of:-

(a) cation exchange resin; and

(b) acrylic and/or styrenic anion exchange resin; resin (b) being present in an amount of 0.5% to 20% by volume, based on the total volume of (a) plus (b), and the level of organic material leached from the resin mixture into the treated liquid is maintained at an acceptable level.



11. A process for treating a liquid to remove cations therefrom substantially as hereinbefore described with reference to any one of the Examples.

DATED THIS 5th day of February, 1990.

ROHM AND HAAS COMPANY

By its Patent Attorneys:

DAVIES & COLLISON

