

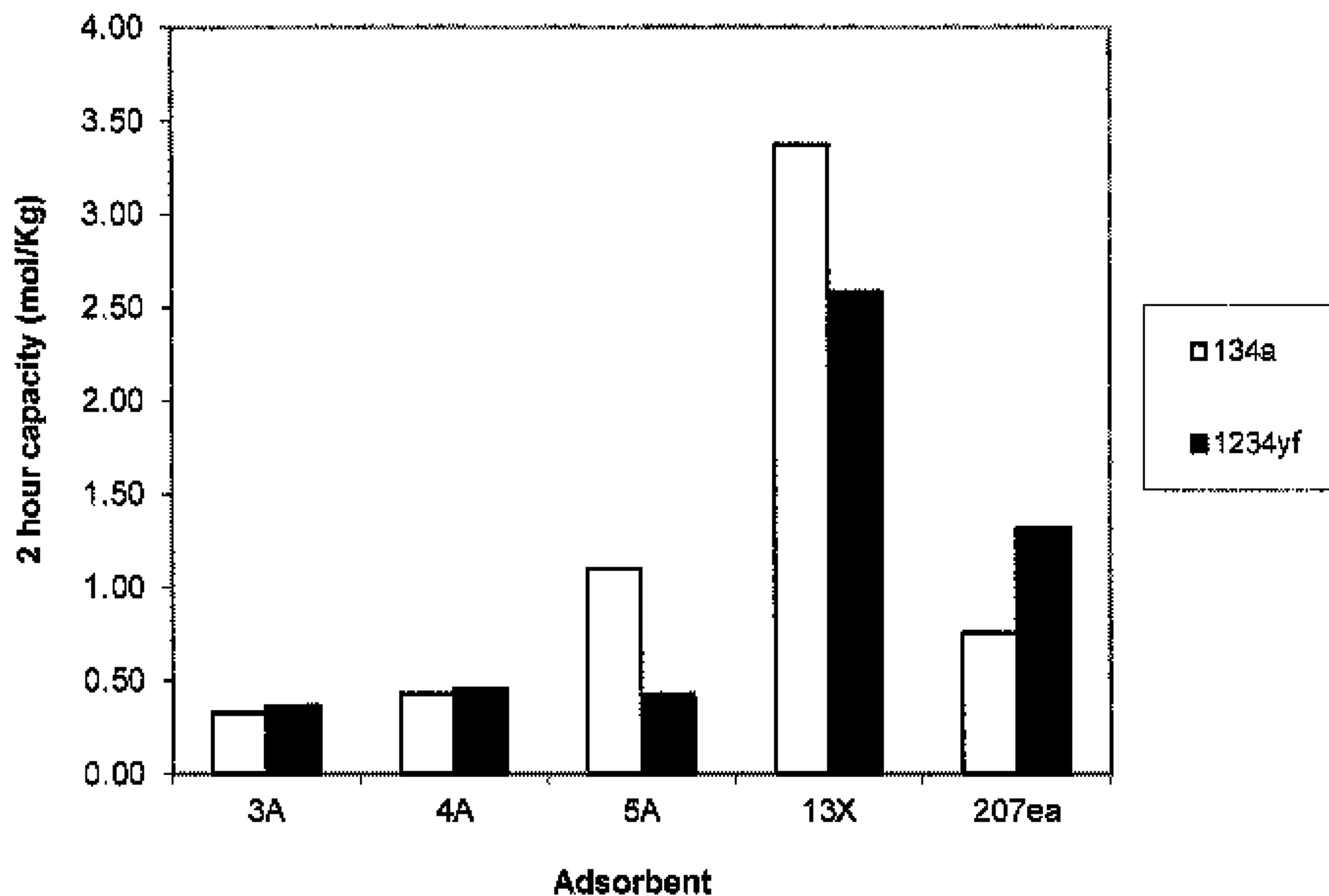


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 (72) Inventeurs/Inventors:  
SHARRATT, ANDREW, GB;  
LOW, ROBERT, GB  
 (73) Propriétaire/Owner:  
MEXICHEM FLUOR S.A. DE C.V., MX  
 (74) Agent: BERESKIN & PARR LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : PROCÉDE DE PURIFICATION DE (HYDRO)FLUOROPROPENES CONTAMINÉS PAR DE L'ETHANE HALOGENÉ  
 (54) Title: PROCESS FOR PURIFYING (HYDRO)FLUOROPROPENES CONTAMINATED WITH HALOGENATED ETHANE

**Refrigerant adsorption**



(57) **Abrégé/Abstract:**

A process for treating a composition comprising one or more desired (hydro)fluoroolefins and one or more undesired halogenated ethanes, halogenated methanes or mixtures thereof so as to reduce the concentration of at least one undesired halogenated ethane or halogenated methane, the process comprising contacting the composition with an adsorbent comprising pores having openings which have a size across their largest dimension of about 6 Å or less.

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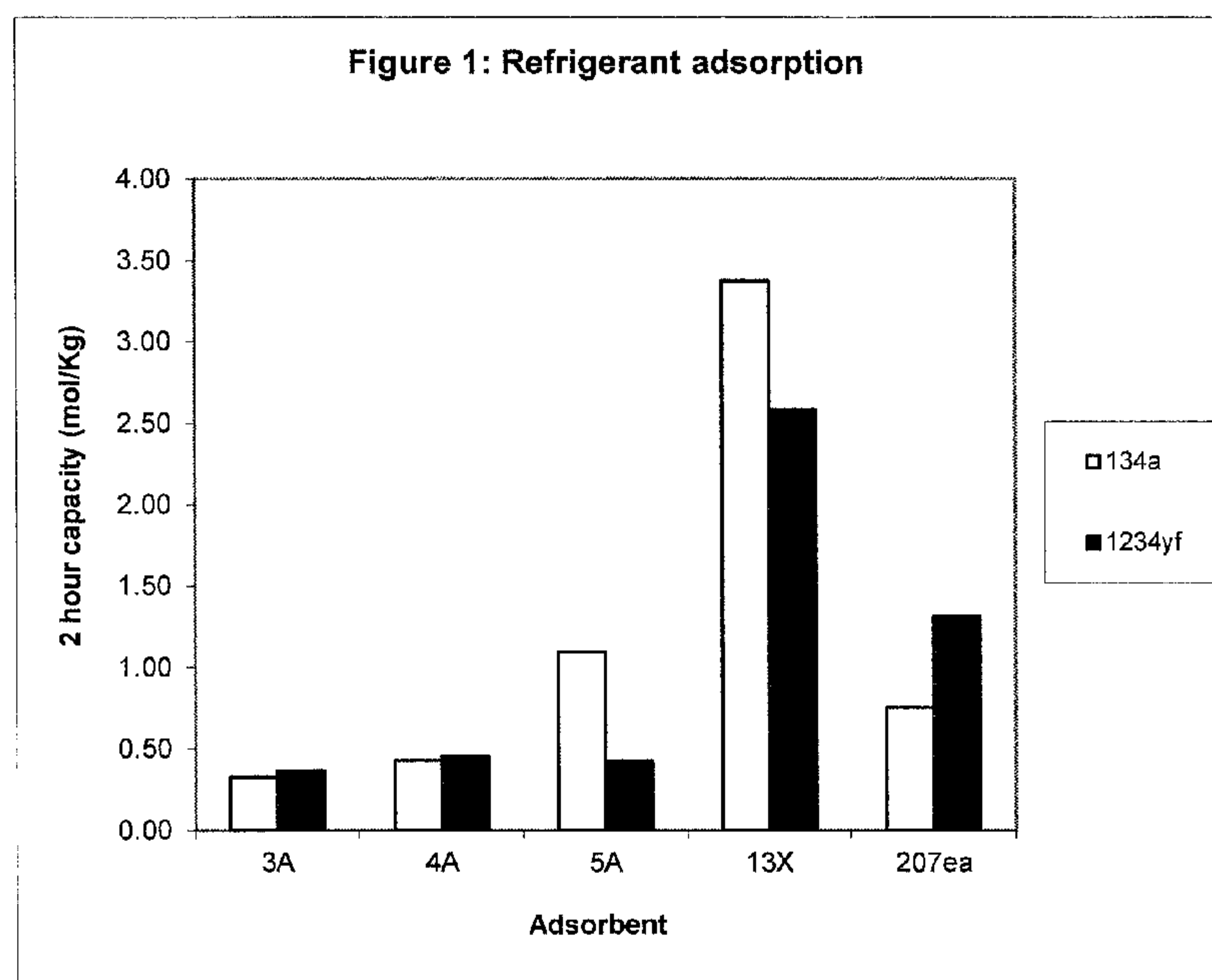
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- (71) **Applicant: MEXICHEM AMANCO HOLDING S.A. DE C.V.** [MX/MX]; Rio san Javier No. 10, Fraccionamiento, Viveros del Rio, Estado de Mexico c.p. 54060, Tlalnepantla (MX).
- (71) **Applicant (for MG only): MEXICHEM UK LIMITED** [GB/GB]; The Heath Business & Technical Park, Runcorn, Cheshire WA7 4QX (GB).
- (72) **Inventors: SHARRATT, Andrew;** Mexichem UK Limited, The Heath Business & Technical Park, Runcorn Cheshire WA7 4QX (GB). **LOW, Robert;** Mexichem UK Limited, The Heath Business & Technical Park, Runcorn Cheshire WA7 4QX (GB).
- (74) **Agent: PUGH, Robert Ian;** POTTER CLARKSON LLP, The Belgrave Centre, Talbot Street, Nottingham Nottinghamshire NG1 5GG (GB).
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(54) **Title:** PROCESS FOR PURIFYING (HYDRO)FLUOROPROPENES CONTAMINATED WITH HALOGENATED ETHANE

(57) **Abstract:** A process for treating a composition comprising one or more desired (hydro)fluoroolefins and one or more undesired halogenated ethanes, halogenated methanes or mixtures thereof so as to reduce the concentration of at least one undesired halogenated ethane or halogenated methane, the process comprising contacting the composition with an adsorbent comprising pores having openings which have a size across their largest dimension of about 6 Å or less.

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## PROCESS FOR PURIFYING (HYDRO)FLUOROPROPENES CONTAMINATED WITH HALOGENATED ETHANE

This invention relates to a process for purifying (hydro)fluoroolefins.

5 The listing or discussion of background information or an apparently prior-published document in this specification should not necessarily be taken as an acknowledgement that the information or document is part of the state of the art or is common general knowledge.

10 (Hydro)halocarbons are typically used as refrigerant or propellant materials. Over the last 20 years, the variety of (hydro)halocarbons used in these applications has changed in view of environmental concerns.

Dichlorodifluoromethane (refrigerant R-12) possesses a suitable combination of  
15 desirable refrigerant properties, and was for many years the most widely used refrigerant. Due to international concern that fully and partially halogenated chlorofluorocarbons were damaging the earth's protective ozone layer, there was general agreement that their manufacture and use should be severely restricted and eventually phased out completely. The use of dichlorodifluoromethane was phased  
20 out in the 1990's.

1,1,1,2-tetrafluoroethane (R-134a) was introduced as an alternative replacement  
refrigerant for R-12, particularly for mobile air-conditioning. However, despite having  
no significant ozone depletion potential, R-134a has a global warming potential (GWP)  
25 of 1300.

In response to this, (hydro)fluoroolefins are increasingly being considered as working  
fluids in applications such as refrigeration, heat pumping, foam blowing, propellants  
and flame retardants. 2,3,3,3-tetrafluoropropene (R-1234yf), which has a GWP of 4,  
30 has been identified as a candidate alternative refrigerant to replace R-134a in certain applications, notably in mobile air-conditioning or heat pumping applications.

As the next generation of low-GWP (hydro)fluoroolefins are adopted across a wide  
range of systems, mixtures of (hydro)fluoroolefins and previous refrigerants, such as  
35 R-134a, are expected to occur during the recovery and recycling of refrigerants. For example, contamination of a (hydro)fluoroolefin with R-134a may be expected when the (hydro)fluoroolefin is used in a system which previously utilised R-134a.

The comparatively higher cost and reduced availability of such (hydro)fluoroolefins makes the ability to separate such mixtures desirable. For example, in certain applications (e.g. mobile air-conditioning) it may not be tolerable or permissible to  
5 return a low-GWP component to a system if it is contaminated with significant levels of high-GWP refrigerant, i.e. R-134a.

However, the separation of such (hydro)fluoroolefins from undesired halogenated ethanes and methanes can be difficult and unattractive. For example, R-134a forms a  
10 minimum boiling azeotrope with R-1234yf, making distillation difficult. As the composition of such an azeotrope varies to some extent with system pressure, a twin column distillation system could be employed in order to separate the two components. However, such a system would be very expensive to build, and complex to operate. The use of a complex distillation system is also not an attractive option for the wider  
15 refrigerant supply chain, such as use by service contractor companies or refrigerant distributors.

The subject invention addresses the above deficiencies by providing a means for such  
20 a separation.

In a first aspect, the invention provides a process for treating a composition comprising one or more desired (hydro)fluoroolefins as a major component and one or more undesired halogenated ethanes, halogenated methanes or mixtures thereof so as to reduce the concentration of at least one undesired halogenated ethane or halogenated  
25 methane, the process comprising contacting the composition with an adsorbent comprising pores having openings which have a size across their largest dimension of about 6 Å or less, for example so as to retain at least a portion of the ethanes and/or methanes in said adsorbent.

30 The inventors have surprisingly found that the use of an adsorbent comprising pores having openings which have a size across their largest dimension of about 6 Å or less is highly selective in retaining undesired halogenated ethanes and/or methanes compared to (hydro)fluoroolefins.

35 In an second aspect of the invention, there is provided a method for recovering a desired component of a spent refrigerant, the method comprising optionally removing a refrigerant from the refrigerant system and contacting the refrigerant with an

adsorbent comprising pores having a size opening across their largest dimension of 6 Å or less to remove or reduce the concentration of one or more undesired components, the desired component comprising a (hydro)fluoroolefin, the undesired component comprising a halogenated ethane and/or halogenated methane, for example such that  
5 at least a portion of the ethanes and/or methanes are retained in said adsorbent.

In a third aspect of the invention, there is provided a kit for recovering a desired component of a spent refrigerant, the kit comprising an apparatus comprising an adsorbent comprising pores having a size opening across their largest dimension of 6  
10 Å or less and instructions for removing the refrigerant from the refrigerant system and contacting the refrigerant with the apparatus to remove or reduce the concentration of one or more undesired components, the desired component comprising a (hydro)fluoroolefin, the undesired component comprising a halogenated ethane and/or halogenated methane, for example such that at least a portion of the ethanes and/or  
15 methanes are retained in said adsorbent.

Preferably, the desired (hydro)fluoroolefin comprises at least 10wt%, for example at least 20wt%, at least 30wt%, at least 40wt%, at least 50wt%, at least 60wt%, at least 70wt%, at least 80wt% or at least 90wt% of the composition or refrigerant to be treated.  
20

In some embodiments the adsorbent comprises pores having openings which have a size across their largest dimension in the range of from about 4 Å to about 6 Å.

In an embodiment the adsorbent comprises pores having openings which have a size  
25 across their largest dimension of about 5 Å.

Preferably, the adsorbent is a molecular sieve, such as a zeolite.

In a preferred embodiment the desired (hydro)fluoroolefin is a (hydro)fluoropropene,  
30 for example a tetrafluoropropene, preferably 2,3,3,3-tetrafluoropropene (R-1234yf). In other embodiments, the tetrafluoropropene may include, say, 1,3,3,3-tetrafluoropropene, preferably E-1,3,3,3-tetrafluoropropene.

In an embodiment, the at least one undesired halogenated ethane or halogenated  
35 methane is a halogenated ethane. In preferred embodiments, the halogenated ethane is a fluorinated ethane such as a tetrafluoroethane, preferably 1,1,1,2-tetrafluoroethane (R-134a).

The contacting step of the process should be conducted at a temperature that allows adsorption to occur. The process is preferably performed, at least in part, at a temperature of from about 0 °C to about 200 °C, such as from about 20 °C to about 100 °C. In some preferred embodiments, the process is performed, at least in part, at a temperature from about 20 °C to about 60 °C, preferably at a temperature of about 40 °C.

The contacting step of the process may be conducted at a pressure sufficient to keep the components of the composition in the liquid or gas phase as appropriate. In a preferred embodiment, the contacting step is conducted at a pressure of from about 0.1 MPa to the saturation pressure.

The process may further comprising an adsorbent treatment step prior to the contacting step. Such an adsorbent treatment step may comprise a heat treatment step, preferably comprising heating the adsorbent to a maximum temperature of at least 150 °C, preferably at least 200 °C, for example at least 300 °C or at least 400 °C.

The heat treatment step may preferably comprise heating the adsorbent to the maximum temperature at a rate of from 1 °C/minute to 100 °C/minute, such as 10 °C/minute to 60 °C/minute, preferably at a rate of from 20 °C/minute to 40 °C/minute. In an embodiment, the heat treatment step comprises maintaining the adsorbent at or around the maximum temperature for a time of from 1 second to 1 hour.

In a further embodiment, the adsorbent treatment step comprises an exposure step comprising exposing the adsorbent to one or more inert gases, preferably N<sub>2</sub> or one or more noble gases, preferably wherein the exposure step is performed before, during or after the heat treatment step. Preferably, the exposure is performed during at least part of the heat treatment step.

The process typically removes at least 50% by weight, preferably 90% by weight, even more preferably 98% of the undesired halogenated ethanes, halogenated methanes or mixtures thereof. In some embodiments, the process reduces the concentration of the undesired halogenated ethanes, halogenated methanes or mixtures thereof to levels at, around or below the limit of detection by gas chromatography.

In an embodiment the adsorbent is dried before use, preferably to a level wherein the moisture content of the adsorbent is less than about 1.5% by weight. Alternatively, the adsorbent may be used in the form it is obtained from the manufacturer.

5 Typically, the process is conducted by passing the composition, at least once, through a polishing bed, such as a granulated solid sorbent bed, containing the adsorbent. In an embodiment the composition is passed through two or more polishing beds. The polishing bed may comprise a packed or fluidised bed.

10 It should be appreciated that a composition to be treated may be contacted with the adsorbent more than once. In such a process the composition may be subjected to repeated contacts with one or more types of adsorbent. Repeated contact will further reduce the content of undesired halogenated ethanes and/or methanes.

15 Typically, the composition to be treated may be contacted with the adsorbent as many times as necessary to remove a sufficient quantity of the undesired halogenated ethanes and/or methanes. The number of times that a composition is contacted with the adsorbent depends on a number of factors, such as the freshness of the adsorbent and the initial level of impurities.

20

The process of the invention may further comprising a step of regenerating the adsorbent after it has been contacted with the composition.

The regeneration step may be carried out through the use of a temperature change.

25 In such a regeneration step, the adsorbent may be regenerated by raising the temperature of the adsorbent and purging it with a hot inert gas, typically the gas will be passed in an opposite direction to that of the composition. It will be appreciated that such a regeneration step must provide sufficient energy to raise the vessel, adsorbent and adsorbate to the desorption temperature, provide the heat of desorption  
30 and (if necessary) raise the adsorbent and the vessel to the regeneration temperature.

The regeneration step may comprise subjecting the adsorbent to a change in pressure. In such a regeneration step, the adsorbent may be regenerated by reducing the partial pressure of the adsorbate. This can be achieved by reducing the total pressure of the  
35 system, introducing an inert gas while total system pressure is maintained, or a combination of the two.

If desired, the process may further comprise one or more additional purifying steps, which may be conducted before and/or after the contacting step. Such an additional step may comprise the use of one or more molecular sieves, preferably wherein the one or more molecular sieves are acid stable. The additional purifying steps may  
5 comprise the use of drying agents and/or distillation techniques.

The process of the invention is carried out, at least in part, in the gas or liquid phase.

The present invention is now illustrated, but not limited by, the following description  
10 and Examples, with reference to the following drawings:

Figure 1 shows a chart representing the 2 hour absorption capacity of a range of absorbent materials for each of the refrigerants R-134a, 1234yf and E-1234ze;

15 Figure 2 shows a chart representing the heat of absorption for a range of absorbent materials for each of the refrigerants R-134a, 1234yf and E-1234ze.

As described above, the invention provides a method for the separation of one or more undesired halogenated ethanes and/or methanes from a composition comprising one  
20 or more desired (hydro)fluoroolefins as a major component. Such a method serves to reduce the concentration of at least one undesired halogenated ethane or halogenated methane through the retention by the absorbent of at least a portion of the halogenated ethanes and/or methanes. The process comprises contacting the composition with an adsorbent comprising pores having openings across their largest dimension of about  
25 6 Å or less, preferably between 4 Å and 6 Å, (also referred to as 'nominal pore diameter').

A particularly preferred variety of adsorbent is a zeolite molecular sieve material preferably having a pore size across its largest dimension of approximately 5 Å,  
30 however alternative molecular sieve materials having similar pore dimensions may also be effective.

The use of such an adsorbent is unexpectedly selective in retaining, within the adsorbent, undesired halogenated ethanes and/or methanes from a composition  
35 comprising desired (hydro)fluoroolefins as a major component.

A composition to be treated may be contacted with a granulated solid sorbent bed comprising the adsorbent. Such a contacting step may be conducted as part of a “once through” process, wherein the product composition is recovered after being contacted with the adsorbent.

5

Alternatively, the composition to be treated may be contacted with a single granulated solid sorbent bed, comprising the adsorbent, multiple times as part of a cyclic process. In which case the sorbent may be regenerated through a change in temperature or pressure as described above, prior to the composition being re-contacted.

10

Twin or multi sorbent bed schemes may also be adopted in order to work the process. In two or multi bed schemes, one or more temperature changes as described above may be employed in order to regenerate the sorbent after each time the composition has been contacted with the sorbent bed. Such processes are known also as “temperature-swing processes”. For example, in a two bed temperature swing process, the second bed becomes operational while the first is regenerated, and vice-versa. It will be appreciated that for the process to be continuous, the regeneration time will be equal to the adsorption time so that the composition feed stream can be switched between the beds.

20

Alternatively, in a two or multi bed scheme, one or more pressure changes, as described above, may be employed to regenerate the sorbent after each contacting step, known also as “pressure-swing” processes. Similarly to temperature swing processes, the composition feed may be switched between beds. As pressure changes can typically be effected more quickly than temperature changes, cycle times can be significantly quicker than temperature swing processes.

25

The process of the invention may be used in preparative chromatographic separation processes.

30

The processes of invention may be used in numerous applications.

The invention may be employed as part of the synthesis and/or purification of desired (hydro)fluoroolefins, in order to remove unwanted by-products or impurities, such as halogenated ethanes and/or halogenated methanes that could be present in the final product.

35

Alternatively, the invention may be employed in order to recover and/or purify a refrigerant that has been used in a system to replace an undesired halogenated ethane or methane refrigerant.

5 Where the invention is used to recover and/or purify a refrigerant as previously discussed, the invention may be used *in situ* in the refrigeration apparatus, e.g. a mobile air-conditioning unit. Alternatively, the invention may be operated in a separate apparatus in which the composition to be treated is introduced to the apparatus.

10 The invention may also form part of a kit for recovering a desired component of a spent refrigerant in which the kit comprises an apparatus comprising an adsorbent comprising pores having a size opening across their largest dimension of 6 Å or less, and instructions for removing the refrigerant from the refrigerant system and contacting the refrigerant with the apparatus to remove or reduce the concentration of one or more  
15 undesired components.

In a further aspect, the invention provides a heat transfer fluid comprising at least one desired (hydro)fluoroolefin as described above and being substantially free of any undesired halogenated methanes or ethanes, the at least one (hydro)fluoroolefin  
20 having been purified by a method as described above.

In another aspect, the invention provides a heat transfer device comprising a heat transfer fluid comprising one or more desired (hydro)fluoroolefins and an adsorbent comprising pores having openings which have a size across their largest dimension of  
25 about 6 Å or less. Preferably, the heat transfer device is a refrigeration system.

### Examples

30

In the following Examples, industrial grade R-1234yf and R-134a was obtained from Apollo Scientific limited and Mexichem. The adsorbents were obtained from Aldrich and Chemviron.

35 *Examples 1 to 10*

The uptake of gas phase adsorbates by adsorbents in real time was measured by TGA analyser. The following adsorbents were tested:

Molecular sieve 3A – pores having openings which have a size across their largest dimension of about 3 Å;

5 Molecular sieve 4A – pores having openings which have a size across their largest dimension of about 4 Å;

Molecular sieve 5A – pores having openings which have a size across their largest dimension of about 5 Å;

10 Molecular sieve 13X – pores having openings which have a size across their largest dimension of about 10 Å;

and Chemviron 207ea activated charcoal.

A small sample (approximately 50 mg) of each adsorbent was accurately weighed into a 100 µL aluminium crucible before being loaded into the TGA furnace.

15

The adsorbent was first pre-treated by being equilibrated at 30 °C under nitrogen (75 mL/min) for 5 minutes, before being heated to 450 °C at 30 °C/minute under flowing nitrogen (75 mL/min). The sample was held at 450 °C for 5 minutes, before being cooled to 40 °C at a rate of 30 °C/minute, and being equilibrated at 40 °C for 5 minutes,  
20 all under a flow of nitrogen (75 mL/min).

The adsorbents were then exposed to 3.3% v/v refrigerant (R-1234yf or R-134a) in nitrogen (75 mL/min), at 40 °C for 120 minutes.

25 The results are shown in Table 1, with Figures 1 and 2 illustrating the capacity of the adsorbents and the heat of adsorption in each case.

As can be seen from the Table and Figures, adsorbents comprising pores having openings which have a size across their largest dimension of below about 6 Å,  
30 particularly between 4 Å and 6 Å, show surprising selectivity for the halogenated ethane over the (hydro)fluoroolefin. This indicates the proficiency of such adsorbents for separating halogenated ethanes from (hydro)fluoroolefins.

Reference Example	Adsorbent	Adsorbate	Wt (mg)	Conc (v/v)	rying wt los (mg)	Dry wt (mg)	Wt gain (mg)	Capacity (% wt)	Capacity (mol/Kg)	Equilibrium	Exotherm (mj)	$\Delta H_{(ads)}$ (kJ/mol)
1	3A	134a	58.6	3.3	9.1937	49.4063	1.6507	3.34	0.33	No	137.65	8.5
2	4A	134a	55.8	3.3	5.3326	50.4674	2.2154	4.39	0.43	No	239.68	11
3	5A	134a	54.2	3.3	8.1745	46.0255	5.1451	11.18	1.1	No	330.82	6.6
4	13X	134a	49.7	3.3	12.2144	37.4856	12.8923	34.39	3.37	Yes	3447.79	27.3
5	207ea	134a	34.2	3.3	0.9434	33.2566	2.5564	7.69	0.75	Yes	339.64	13.6
6	3A	1234yf	56.3	3.3	9.8521	46.4479	1.9397	4.18	0.37	No	62.18	3.3
7	4A	1234yf	53.3	3.3	10.873	42.427	2.1945	5.17	0.45	No	72.99	3.4
8	5A	1234yf	59.7	3.3	11.0719	48.6281	2.3742	4.88	0.43	No	88.19	3.8
9	13X	1234yf	47.1	3.3	11.726	35.374	10.4077	29.42	2.58	Yes	1821.33	17.8
10	207ea	1234yf	31.8	3.3	0.9976	30.8024	4.6035	14.95	1.31	Yes	699.24	15.5

Table 1

Preferences and options for a given aspect, feature or parameter of the invention should, unless the context indicates otherwise, be regarded as having been disclosed in combination with any and all preferences and options for all other aspects, features  
5 and parameters of the invention.

The listing or discussion of an apparently prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge

10

## Claims

1. A process for treating a composition comprising one or more desired tetrafluoropropenes and one or more undesired halogenated ethanes, so as to reduce the concentration of at least one undesired halogenated ethane, the process comprising contacting the composition with an adsorbent comprising pores having openings which have a size across their largest dimension of 6 Å or less.
2. A process according to claim 1 wherein the desired tetrafluoropropene comprises at least 10wt% of the composition to be treated.
3. A process according to claim 2 wherein the desired tetrafluoropropene comprises at least 20wt% of the composition to be treated.
4. A process according to claim 3 wherein the desired tetrafluoropropene comprises at least 30wt% of the composition to be treated.
5. A process according to claim 4 wherein the desired tetrafluoropropene comprises at least 40wt% of the composition to be treated.
6. A process according to claim 5 wherein the desired tetrafluoropropene comprises at least 50wt% of the composition to be treated.
7. A process according to claim 6 wherein the desired tetrafluoropropene comprises at least 60wt% of the composition to be treated.
8. A process according to claim 7 wherein the desired tetrafluoropropene comprises at least 70wt% of the composition to be treated.
9. A process according to claim 8 wherein the desired tetrafluoropropene comprises at least 80wt% of the composition to be treated.
10. A process according to claim 9 wherein the desired tetrafluoropropene comprises at least 90wt% of the composition to be treated.
11. A process according to any one of claims 1 to 10 wherein the adsorbent comprises having openings which have a size across their largest dimension of from 4 Å to 6 Å.

12. A process according to any one of claims 1 to 11 wherein the adsorbent comprises pores having openings which have a size across their largest dimension of 5 Å.
13. A process according to any one of claims 1 to 12 wherein the adsorbent is a  
5 molecular sieve.
14. A process according to any one of claims 1 to 13 wherein the adsorbent comprises a zeolite.
- 10 15. A process according to claim 1 wherein the tetrafluoropropene is 2,3,3,3-tetrafluoropropene (1234yf).
16. A process according to any one of claims 1 to 15 wherein the at least one undesired halogenated ethane is a fluorinated ethane.
- 15 17. A process according to claim 16 wherein the fluorinated ethane is tetrafluoroethane.
18. A process according to claim 17 wherein the tetrafluoroethane is 1,1,1,2-  
20 tetrafluoroethane (134a).
19. A process according to any one of claims 1 to 18 wherein the contacting step is performed at a temperature of from 0 °C to 200 °C.
- 25 20. A process according to claim 19 wherein the contacting step is performed at a temperature of from 20 °C to 100 °C.
21. A process according to claim 20 wherein the contacting step is performed at a temperature from 20 °C to 60 °C.
- 30 22. A process according to claim 21 wherein the contacting step is performed at a temperature of 40 °C.
23. A process according to any one of claims 1 to 22 wherein the contacting step is  
35 conducted at a pressure of from 0.1 MPa to the saturation pressure.
24. A process according to any one of claims 1 to 23 further comprising an adsorbent treatment step prior to the contacting step.

25. A process according to claim 24 wherein the adsorbent treatment step comprises a heat treatment step comprising heating the adsorbent to a maximum temperature of at least 150 °C.
- 5 26. A process according to claim 25 wherein heat treatment step comprising heating the adsorbent to a maximum temperature of at least 200 °C.
27. A process according to claim 26 wherein the heat treatment step comprising heating the adsorbent to a maximum temperature of at least 300 °C.
- 10 28. A process according to claim 27 wherein the heat treatment step comprising heating the adsorbent to a maximum temperature of at least 400 °C.
29. A process according to any one of claims 25 to 28 wherein the heat treatment step  
15 comprises heating the adsorbent to the maximum temperature at a rate of from 1 °C/minute to 100 °C/minute.
30. A process according to claim 29 wherein the heat treatment step comprises heating the adsorbent to the maximum temperature at a rate of from 10 °C/minute to 60 °C/minute.
- 20 31. A process according to claim 30 wherein the heat treatment step comprises heating the adsorbent to the maximum temperature at a rate of from 20 °C/minute to 40 °C/minute.
32. A process according to any one of claims 25 to 31 wherein the heat treatment step  
25 comprises maintaining the adsorbent at or around the maximum temperature for a time of from 1 second to 1 hour.
33. A process according to any one of claims 23 to 31 wherein the adsorbent treatment  
30 step comprises an exposure step comprising exposing the adsorbent to one or more inert gases.
34. A process according to claim 33 wherein the inert gases are selected from N<sub>2</sub> or one or more noble gases.
- 35 35. A process according to claim 33 or 34 wherein the exposure step is performed before, during or after the heat treatment step.

36. A process according to any one of claims 1 to 35 wherein the process removes at least 50% by weight of the undesired halogenated ethanes.
37. A process according to claim 36 wherein the process removes at least 90% by weight of the undesired halogenated ethanes.
38. A process according to claim 37 wherein the process removes at least 98% by weight of the undesired halogenated ethanes.
39. A process according to any one of claims 1 to 38 wherein the adsorbent is dried before use.
40. A process according to any one of claims 1 to 39 wherein the moisture content of the adsorbent is less than 1.5% by weight.
41. A process according to any one of claims 1 to 40 wherein the composition to be treated is passed, at least once, through a polishing bed containing the adsorbent.
42. A process according to claim 41 wherein the composition is passed through two or more polishing beds.
43. A process according to claim 41 or 42 wherein the polishing bed comprises a packed or fluidised bed.
44. A process according to any one of claims 1 to 43 wherein the composition is contacted with the adsorbent more than once.
45. A process according to any one of claims 1 to 44 further comprising a step of regenerating the adsorbent after it has been contacted with the composition.
46. A process according to claim 45 wherein the regenerating step comprises contacting the adsorbent with a heated stream of inert gas and/or heating the adsorbent whilst the or an inert gas is passed over it.
47. A process according to claim 45 or 46 wherein the regenerating step comprises subjecting the adsorbent to a change in pressure.
48. A process according to any one of claims 1 to 47 further comprising one or more additional purifying steps, which are conducted before and/or after the contacting step.

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49. A process according to claim 48 wherein the additional purifying step comprises the use of one or more molecular sieves.
50. A process according to claim 49 wherein the one or more molecular sieves are acid  
5 stable.
51. A process according to any one of claims 48 to 50 wherein the additional purifying step comprises the use of drying agents and/or distillation techniques.
- 10 52. A process according to any one of claims 1 to 51 which is carried out in the gas or liquid phase.
53. A method for recovering a desired component of a spent refrigerant, the method comprising removing the refrigerant from a refrigerant system and contacting the  
15 refrigerant with an adsorbent comprising pores having a size opening across their largest dimension of 6 Å or less to remove or reduce the concentration of one or more undesired components, the desired component comprising a tetrafluorofluoropropene, the undesired component comprising a halogenated ethane.
- 20 54. A method according to claim 53 wherein the desired tetrafluoropropene comprises at least 10wt% of the spent refrigerant.
55. A method according to claim 54 wherein the desired tetrafluoropropene comprises at least 20wt% of the spent refrigerant.
- 25 56. A method according to claim 55 wherein the desired tetrafluoropropene comprises at least 30wt% of the spent refrigerant.
57. A method according to claim 56 wherein the desired tetrafluoropropene comprises  
30 at least 40wt% of the spent refrigerant.
58. A method according to claim 57 wherein the desired tetrafluoropropene comprises at least 50wt% of the spent refrigerant.
- 35 59. A method according to claim 58 wherein the desired tetrafluoropropene comprises at least 60wt% of the spent refrigerant.

60. A method according to claim 59 wherein the desired tetrafluoropropene comprises at least 70wt% of the spent refrigerant.

5 61. A method according to claim 60 wherein the desired tetrafluoropropene comprises at least 80wt% of the spent refrigerant.

62. A method according to claim 61 wherein the desired tetrafluoropropene comprises at least 90wt% of the spent refrigerant.

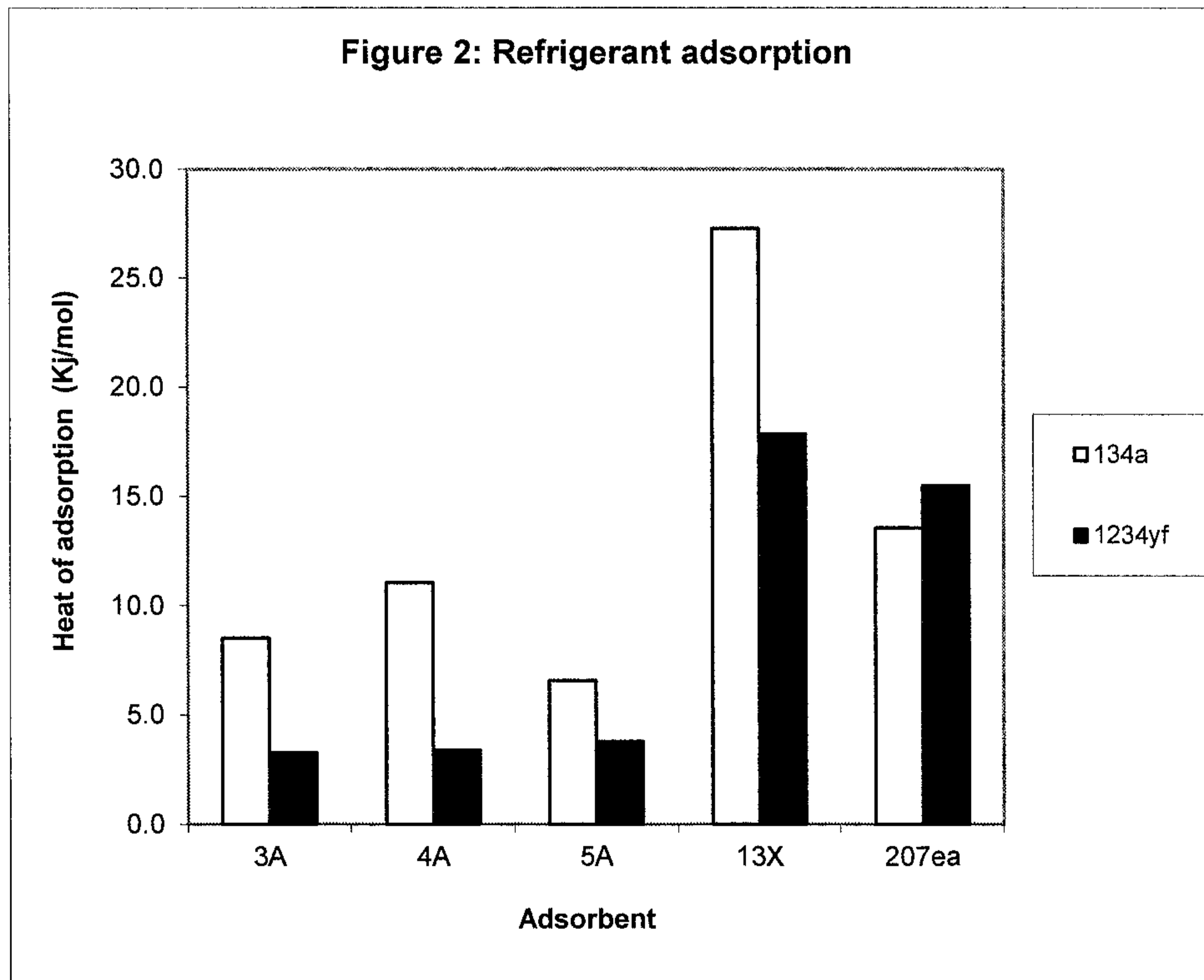
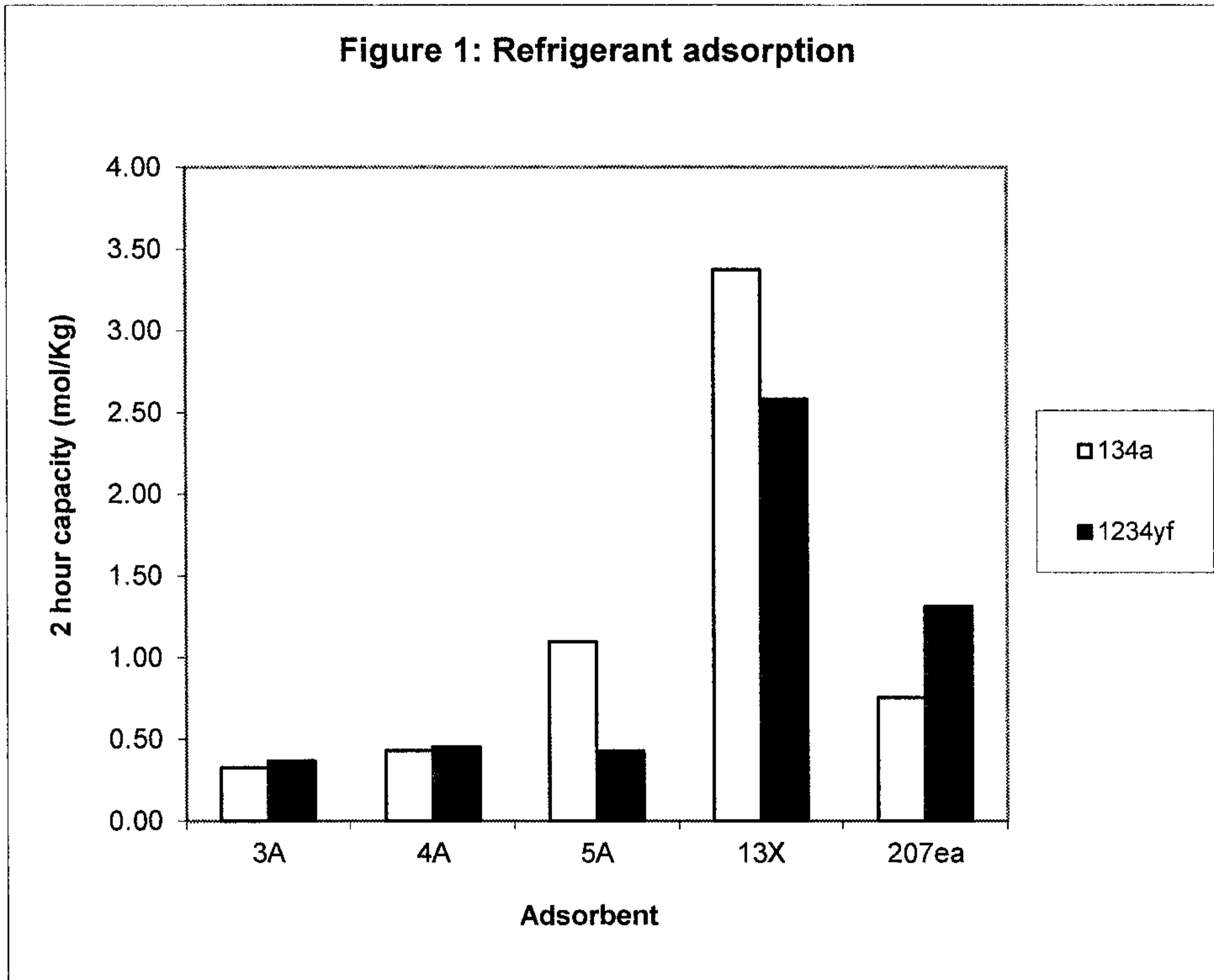
10 63. A kit for recovering a desired component of a spent refrigerant, the kit comprising an apparatus comprising an adsorbent comprising pores having a size opening across their largest dimension of 6 Å or less and instructions for removing the refrigerant from the refrigerant system and contacting the refrigerant with the apparatus to remove or reduce the concentration of one or more undesired components, the desired component  
15 comprising a tetrafluoropropene, the undesired component comprising a halogenated ethane.

64. A heat transfer device comprising a heat transfer fluid comprising one or more desired tetrafluoropropenes and an adsorbent comprising pores having openings which  
20 have a size across their largest dimension of 6 Å or less.

65. A heat transfer device according to claim 64 wherein the heat transfer device is a refrigeration system.

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# Refrigerant adsorption

