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(54) Removal of metal ions from aqueous medium using a cation-exchange resin having water-insoluble compound dispersed therein.

(57) Metal ions such as divalent radium are removed from an aqueous medium by contacting the aqueous medium with a resin particulate composed of a cation-exchange resin and a water-insoluble compound such as barium sulfate dispersed in the resin.

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REMOVAL OF METAL IONS FROM AQUEOUS MEDIUM USING A CATION-EXCHANGE RESIN HAVING WATER-INSOLUBLE COMPOUND DISPERSED THEREIN

This invention relates to water-insoluble, hydrophilic resins that can remove metal ions, such as radium, from an aqueous medium.

In many industries that employ aqueous streams containing metal ions, it is necessary to remove such ions from such streams because such metal ions are valuable and/or extremely toxic. Exemplary industries are those employing aqueous streams containing radioactive metal ions such as radium, e.g., industries using atomic reactors, hospitals, municipalities, scientific laboratories and industries engaged in mining of valuable metals.

For example, in the removal of naturally occurring radium and/or barium from public water supplies, it has been a practice to use the various water softening procedures, including the use of ion-exchange softening plants as well as lime softening plants. Removal efficiencies range from 70 percent up to about 98 percent for these procedures. Unfortunately, however, workers in such plants removing radium are exposed to increased levels of radiation. Also, such processes yield significant quantities of radioactive wastes that must be properly stored.

In the mining of uranium it is often necessary to remove and dispose of substantial quantities of aqueous liquids containing low levels of radionuclides such as uranium and radium. The composition of this aqueous liquid may be either acidic or alkaline, depending upon (1) the particular uranium material being mined, (2) the other minerals present in the host formation, and (3) the chemical composition of the ground water itself. During the recovery of the desired uranium, it is found that the undesired radioactive metals are often absorbed on slimes which are then passed to tailings impoundment areas. Unfortunately, water contacting such areas becomes contaminated with such radioactive metals and must be processed to remove the radioactive metals before discharge.

Similarly, the accumulation of radioactive materials in other aqueous streams, as well as on the equipment through which they are passed, creates real problems of handling such streams and in their disposal for a wide variety of industries, e.g., the treatment of mine water and hospital waste streams.

In the past, such aqueous streams containing radioactive metals or other metals have been purified with various ion-exchange systems. Unfortunately, however, such exchange systems are expensive in that they have to be frequently regenerated. Moreover, such regeneration gives rise to further aqueous liquids containing radioactive metals or other metals which are often toxic and/or valuable. Alternatively, it has been a practice to precipitate the metals from such aqueous streams by the addition of various chemical reagents. The resulting precipitate forms a sludge at the bottom of the precipitating pond, thereby causing long-term disposal problems. Since the precipitants are not readily filtered, large installations would be required in order to facilitate proper disposal of the precipitate. Unfortunately, the foregoing methods are not specific for the removal of metal ions desired to be removed. As a result, unwanted metal ions such as sodium, calcium and magnesium, which are often present in large quantities in such aqueous streams, must be handled as well. In the case of ion-exchange systems, the ion-exchange systems quickly become saturated with such unwanted metal ions and regeneration must occur more frequently than would otherwise be required.

As disclosed in U.S. Patents 2,961,399 (Alberti, November 22, 1960) and 4,054,320 (Learmont, October 18, 1977), it is well recognized that various forms of barium, particularly barium sulfate, are relatively effective for the removal of many metals, particularly radium and other metals such as strontium, cerium, ruthenium and antimony from aqueous media. Unfortunately, these procedures often produce substantial amounts of sludges containing radioactive or other metals that must be disposed of or cleaned.

In view of the aforementioned deficiencies of prior art techniques for removal of radioactive materials from aqueous media, it is highly desirable to provide an effective means for removal of metal ions, particularly radioactive and/or toxic metal ions from aqueous media, which means does not generate significant volumes of radioactive and/or toxic wastes in the process, and which reduces the amount of metal ion in the treated aqueous media to very low levels.

The present invention is a finely divided particulate for removing metal ions from an aqueous medium characterized in that the particles of the particulate comprise (1) a porous matrix of a water-insoluble, hydrophilic, normally solid, organic polymer bearing a plurality of pendant anionic moieties and (2) dispersed in said matrix, a water-insoluble inorganic compound capable of removing metal ions from an aqueous medium, said particles being permeable to the passage of the metal ions from the aqueous medium under conditions such that a substantial portion of said metal ions are removed from the aqueous medium and retained in the matrix when the particles are contacted with the aqueous medium.

The present invention is also a process for preparing an adsorptive resin for removing and retaining metal ions from an aqueous medium characterized by (1) contacting finely divided particles of a water-insoluble, hydrophilic polymer bearing pendant anionic moieties in the interior regions of the particles with an aqueous solution of a compound of a similar metal under conditions such that a salt of the metal and a desired portion of the anionic moieties in said interior regions are formed and (2) contacting the resulting metal salt form of the particles with a reactant under conditions such that (a) the reactant invades said interior regions and reacts with the similar metal to form a water-insoluble compound capable of removing the desired metal ion from an aqueous medium and (b) the resulting particles containing the water-insoluble compound are permeable to the the transport of metal ions into the interior regions of the particles.

In a further aspect, this invention is a method for removing metal ions from an aqueous liquid which comprises contacting the particulate described above with the aqueous liquid under conditions such that the metal ions pass into the interior regions of the particles of the resin and are thereby removed from the aqueous liquid.

Surprisingly, the adsorptive resins of the present invention are much more efficient in removing specific metal ions from aqueous medium than the particulate adsorbents of the prior art. By "more efficient" is meant that the resins have the capacity to remove and retain greater quantities of specific metal ions and can reduce the concentration of such specific metal ions in the aqueous media to lower levels than can the prior art absorbents. Also surprising is the substantial capacity of such adsorptive resins to remove and retain the specific metal ions from aqueous media containing other metal ions as well. Finally, the adsorptive resins are easily handled and more readily disposed of than are prior art absorbents.

The absorptive resins of the present invention are particularly useful in removing radioactive divalent radium ions from aqueous effluents of uranium mining operations, especially those containing rather low levels, e.g., 2-1000 picocurries/liter, of the radium ions. Other uses for the resins of the present invention include those requiring the removal of radium from leach solutions of various mining processes, as well as from uranium tailing streams, and a wide variety of applications that require dense resins for the removal of cations from aqueous liquids. Examples of such applications are the processing of dense solutions, e.g., concentrated sugar solutions and salt solutions, by conventional downflow or upflow techniques. In addition, by using fluidized bed ion--exchange procedures with these dense resins, a more efficient operation can be achieved.

The hydrophilic polymer forming the porous matrix of the particulate is suitably any normally solid, water-insoluble organic polymer bearing a sufficient number of pendant anionic moieties to enable the polymer to exchange cations from an aqueous medium. The backbone of the polymer is not particularly critical as long as the resultant polymer containing the anionic moieties is water-insoluble. Accordingly, the polymer may be phenolic, polyethylenic including styrenic and acrylic polymers and others that are capable of exchanging cations, with the cross-linked styrenic polymers being preferred. The type of anionic moieties contained by the polymer are those which will exchange metal ions from an aqueous medium. Typically, suitable anionic moieties include sulfonic, carboxylic and phosphonic, with sulfonic being preferred. The concentration of anionic moieties in the polymer is that concentration which will ensure presence of such moieties in the interior regions of the particles and will enable the polymer to exchange cations from an aqueous medium. Preferably, the concentration of anionic moieties is from about 1 to about 12, and in some cases preferably from about 4.7 to about 5.3, milliequivalents per gram (meq/g) of polymer.

Especially preferred as polymers in the practice of the present invention are cross-linked polymers formed by the addition copolymerization of polymerizable monoethylenically unsaturated monomer or a mixture of such monomer with a cross-linking agent copolymerizable therewith, typically a polyethylenically unsaturated monomer such as divinylbenzene. Suitable polymerizable monoethylenically unsaturated monomers, cross-linking agents, catalysts, polymerization media and methods for preparing the cross-linked addition copolymers in suitable particulate form are well-known in the art. Illustrative of such art are U.S. Patents 2,960,480 and 2,788,331 which teach the preparation of gel-type, cross-linked polymers and U.S. Patents 3,637,535 and 3,549,562 which teach the preparation of more porous resins, often called macroporous resins. Of the known polymerization monoethylenically unsaturated monomers, the monovinylidene aromatic, such as styrene and monoalkyl-substituted styrenes such as vinyl toluene, ethylvinyl benzene and vinyl naphthalene, are preferred, with styrene being especially preferred. Preferred cross-linking agents include polyvinylidene aromatics such as divinyl benzene, divinyl toluene, divinyl xylene, divinyl naphthalene, trivinyl benzene, divinyl diphenyl ether, divinyl diphenyl sulfone and isopropenyl vinyl benzene; ethylene glycol dimethacrylate and divinyl sulfide, with the polyvinylidene aromatics, especially divinyl benzene, being most preferred.

As stated hereinbefore, this matrix polymer contains a plurality of anionic moieties. Preferably, such anionic moieties are sulfonic acid moieties characteristic of any of the conventional sulfonic acid resins that are commercially available for exchanging cations from aqueous solution. Typically, this preferred resin is in sodium salt or acid form. Examples of such exchange resins are the resinous condensation products of formaldehyde and phenol sulfonic acid, cationic exchange resins obtained by sulfonating the resinous condensation products of formaldehyde with phenol or with other monohydric or polyhydric phenols, the sulfonated resinous copolymers of monoethylenically unsaturated monomers and polyethylenically unsaturated monomers such as styrene and divinylbenzene. Especially preferred cationic exchange resins are the sulfonated copolymers of styrene cross-linked with from about 1 to about 20, preferably from about 2 to about 4, weight percent of divinylbenzene. Such especially preferred resins have a sufficient concentration of sulfonic acid moieties to have dry weight capacities in the range from about 4.5 to about 5.2, particularly from about 4.8 to about 5.1, milliequivalents of hydrogen ion per gram of dry resin (meq H^+/g). Such especially preferred resins also have water retention capacities in the range of about 35 to about 90, particularly from about 50 to about 75, weight percent of water in the wet form of the resin. Examples of such especially preferred resins are gel resins in the sodium, hydrogen or lithium form and macroporous and acrylic resins, that are typically in the form of spherical beads.

As stated hereinbefore, the matrix polymer containing the anionic moieties is in the form of a particulate. Preferably, such particulate has an average particle diameter in the range from about 10 to about 1200 micrometers, especially from about 500 to about 1200 micrometers. The particles of such particulate are porous so as to permit the transport of metal ions from an aqueous medium into the interior regions of the particles. For example, such resins preferably have micropores having an average pore size in the range from about 10 to about 2000 Angstrom units, especially from about 20 to about 100 Angstrom units, and a surface area from about 0.005 to about 0.15 square meter per gram of wet resin containing approximately 75 weight percent of water, especially from about 0.005 to about 0.1 square meter per gram.

Suitable matrix polymers having anionic moieties other than sulfonic acid, such as carboxylic acid and phosphonic acid as well as methods for preparing such materials, are described in Ion-Exchange, Helfferich, McGraw-Hill (1962).

The water-soluble compound of the similar metal suitably employed in the practice of this invention is one that (1) is sufficiently soluble such that an aqueous solution of the compound will convert the resin by ion-exchange to the similar metal forms of the resin, (2) reacts with the anionic moieties of the polymer to provide a salt of the metal and a desired portion of the anionic moieties in the interior regions of the particles, and (3) contains a metal similar to the specific metal ion to be removed from the aqueous medium. For the purposes of this invention, a metal is similar to the specific metal ion to be removed from the aqueous medium if the metal will form a water-insoluble compound capable of removing the specific metal ion from aqueous solution and retain the specific metal ion during continued contact with the aqueous medium. Preferably, the similar metal is chemically similar to the specific metal, as predicted by the Periodic Table of elements. Illustratively, the similar metal may be in the same group of the Periodic Table of elements as the specific metal ion, most preferably from a period adjacent to the period of the specific metal ion. In the case of the transition and inner transition metals, the similar metal may be the element adjacent to or nearby the specified metal in the same period of the Periodic Table of elements. For example, where radium is the specific metal ion, the similar metal is preferably barium, with strontium and calcium being less preferred. When gold is the specific metal, the similar metal is preferably silver. Examples of such water-soluble compounds include barium hydroxide and the water-soluble salts of barium such as barium chloride, barium bromide, barium cyanate and barium acetate, with barium hydroxide being especially preferred. Other suitable water-soluble compounds include strontium acetate, strontium chloride, calcium chloride, silver nitrate, calcium acetate and thorium nitrate.

The reactant suitably employed in the practice of this invention is a compound that is capable of (1) invading the interior regions of the particles containing salt moieties of the similar metal cation moieties and the anionic moieties and (2) reacting with the similar metal cation moieties to form a water-insoluble compound that is capable of removing the specific metal cation from an aqueous liquid. This compound is sufficiently water--insoluble and has sufficient affinity for the specific metal ion such that it retains the specific metal ion in the particles of the adsorptive resin after repeated contact with the aqueous liquid. Preferably, this water-insoluble compound is so insoluble in water that less than 2 grams, most preferably less than 0.1 gram, of the compound will dissolve in a liter of water. The reaction of the reactant with the metal form of the wet resin is preferably a strong acid such as sulfuric acid or hydrochloric acid or a moderately strong acid such as phosphoric acid, that will react with the similar metal to form the desired water-insoluble compound. When the similar metal is barium, the reactant is sulfuric acid, iodic acid, gaseous sulfur trioxide and similar acids that are known to react with barium to form water-insoluble salts in highly acidic medium, with rather concentrated sulfuric acid, e.g., from 5M to 16M H_2SO_4, being more preferred and 6M to 10M H_2SO_4 being most preferred. When the similar metal is silver, the reactant is preferably hydrochloric acid or other acid that reacts with silver to form a water-insoluble compound.

In the preparation of the similar metal salt form of the water-insoluble polymer particulate, the polymer particulate containing the anionic moieties in acid or sodium salt form is immersed or otherwise washed with an aqueous solution of a compound of the similar metal, e.g., barium hydroxide, calcium chloride or silver nitrate. The concentration of the aqueous solution of the similar metal compound is not particularly critical as long as a suitable degree of exchange between the similar metal and the anionic moieties of water-insoluble polymer is obtained, particularly in the interior regions of the particles of water-insoluble polymer. Preferably, the concentration of the water-soluble compound of the similar metal is from about 0.1 to about 20, most preferably from 1 to 10, weight percent in the aqueous solution. In general, the procedures used to carry out the exchange to the similar metal salt form of the resins is in accordance with conventional techniques for cation-exchange involving the exchange of similar metal ions from aqueous solution.

The conversion of the similar metal salt form of the resin to the adsorptive resin, which contains the water-insoluble compound of the similar metal that is useful for the removal and retention of the specific metal ions from aqueous solution, is preferably accomplished by passing the reactant throughout the interior regions of the particles containing the salt moieties of the similar metal and the anionic moieties. To ensure the invasion of the interior regions of the polymer particles by the reactant, it is critical that the concentration of reactant be sufficient to overcome the Donnan potential that is characteristic of the particular polymer and anionic moieties involved. If such concentration is not sufficient, it is observed that formation of the water-insoluble compound of the similar metal occurs only on the surfaces of the particle with none being formed within the interior regions of the particle. Such plugged resins are generally undesirable for the practice of this invention. Preferably, in the case where barium is the similar metal, the concentration of sulfuric acid that is used to treat the barium salt form of most conventional cation-exchange resins derived from copolymers of styrene and divinylbenzene is in the range from about 40 to about 90 weight percent, preferably from about 45 to about 65 weight percent.

Following the formation of the water-insoluble compound within the resin particles, it is generally desirable to wash the resin to remove any residual reactant or other undesirable products using deionized water. In the washed form, the resin is ready for use in the removal of specific metal ions from aqueous solutions.

This adsorptive resin comprises particles of a porous matrix polymer having a plurality of anionic moieties and dispersed within said matrix particles a water-insoluble compound capable of removing and retaining metal ions from an aqueous medium. In general, the water-insoluble compound is present in an amount sufficient to increase the capacity of the resin to remove and retain the desired specific metal ions from an aqueous medium by at least 10 weight percent, preferably by at least 100 weight percent, over the capability of the matrix polymer containing no water-insoluble compound. Preferably the adsorptive resin contains from about 1 to about 90, most preferably from about 5 to about 50, weight percent of the water-insoluble compound.

In practice, a liquid aqueous medium containing specific metal ions such as radium, radioactive strontium, cerium, radioactive cobalt, ruthenium, gold or other precious metals, thorium, arsenic, cadmium, chromium, silver, lead and antimony, are contacted with the particulate of this invention under conditions such that the specific metal ions are transported into the interior regions of the particles whereby such specific metal ions are removed from the aqueous solution and retained in the particles. Typically, such contacting is similar to that employed in the exchange of cations from aqueous solution. Concentration of the specific metal ions in the aqueous solution being treated can range from about 0.001 part per trillion to about 10,000 parts per million, preferably from about 0.01 part per trillion to about 1000 parts per million, said parts being based on the weight of the solution.

The following examples illustrate the invention. Unless otherwise indicated, all parts and percentages are by weight.

Example 1

The resin employed was the acid form of a wet 2 percent cross-linked sulfonated styrene/divinylbenzene copolymer cation-exchange resin having particle diameters in the range from 500 to 1200 micrometers, a dry weight capacity of 5.1 milliequivalents of H^+ per dry gram, (meq H^+/g), a water retention capacity of 75.9 percent and a density of 1.13 g/ml. To 200 g of this resin there is added sufficient 0.3 N $Ba(OH)_2$ to quantitatively convert the resin to the barium form and provide a small excess of $Ba(OH)_2$. This barium form of the resin has a water retention capacity of 42 percent and a density of 1.29 g/ml. Following conversion to the barium form, the resin is contacted with a small amount of acid form of the resin to scavenge excess $Ba(OH)_2$. The barium form of the resin is then washed with deionized water and dewatered by filtration. To this dewatered barium form of the resin (barium-resin) is added 6M H_2SO_4 in an amount sufficient to cover the resin and to maintain the concentration of H_2SO_4 at ≥5M H_2SO_4 as approximately 80 percent of the water in the barium-resin is released into solution. The barium-resin shrinks initially by 20-40 percent by volume and after 3-5 hours swells to a volume slightly greater than the barium-resin. Analysis of the resulting resin indicates that the resin has been converted to acid form and $BaSO_4$ has been formed in the interior regions. Excess sulfuric acid is removed by filtration. The filtered resin is washed with deionized water which swells the resin to a volume slightly larger than the original volume in the acid form. The resulting adsorptive resin has a density of 1.216 g/ml, dry weight capacity of 2.9 meq of H^+/dry gram and a water retention capacity of 65 percent.

A 2500-g portion of the resulting adsorptive resin is charged to a column (300 cm x 5.08 cm diameter) to a wet settled bed height of 76 cm. An aqueous medium containing 25 picocurries of radium ion per liter is passed up through two of the aforementioned columns connected in series at a rate of 26 liters/minute for a period of 7 months. The eluate from the column is periodically tested for radioactivity and found to contain less than 2 picocurries of radium per liter during the entire period. The adsorptive resin is then analyzed and found to contain the appropriate quantity of radium ion.

Example 2

Using a cation-exchange resin similar to that of Example 1, except that it has a water retention capacity of 67.9 percent, a cross-link content of 4 percent and a density of 1.11 g/ml, an adsorptive resin is prepared according to the procedure of Example 1 except that 8M H_2SO_4 is substituted for 6M H_2SO_4. The resulting adsorptive resin has a density of 1.301 g/ml, a water retention capacity of 54.6 percent and a dry weight capacity of 3.1 meq H^+/g.

The adsorptive resin is tested for radium removal capability by the procedure described in Example 1 and found to have an effective radium removal capability.

Example 3

Following the procedure of Example 1, a 250-g portion of a wet, 2 percent cross-linked, sulfonated styrene/divinylbenzene copolymer cation-exchange resin having particle diameters in the range from 500 to 1200 micrometers, a dry weight capacity (DWC) of 5.18 meq H^+/g, a water retention capacity (WRC) of 77.3 percent and a density of 1.09 g/ml is contacted with sufficient 0.5 N $Ba(OH)_2$ to quantitatively convert the resin to the barium form. This barium-resin is then contacted with 8-10M H_2SO_4 in an amount sufficient to cover the resin and maintain the concentration of H_2SO_4 at $\geq$5M H_2SO_4. The resulting adsorptive resin is washed with deionized water to remove excess acid and 30 g of the resin is tested for DWC, WRC, percent barium, wet volume capacity in meq H^+

per ml of actual volume of resin (WVC), and density. The results of the tests are reported in Table I.

The adsorptive resin is cycled through the foregoing procedure five additional times and tested for DWC, WRC, percent barium, WVC and density after each cycle.

The results of these tests are reported in Table I. As evidenced by the data in this table, the concentration of barium increases with each additional cycle.

TABLE I

Sample No.	Cycle	DWC, meq H^+/g	WVC, meq H^+/ml vol.	% WRC	Density (g/ml)	% Barium
1	1	2.86	1.17	66.2	1.21	21.9
2	2	2.06	1.14	58.0	1.32	31.0
3	3	1.60	1.10	51.2	1.41	35.7
4	4	1.42	1.14	45.7	1.53	40.0
5	5	1.18	1.07	43.5	1.61	43.0
6	6	1.01	1.01	40.6	1.67	45.1

1. A finely divided particulate for removing metals ions from an aqueous medium characterized in that the particules of the particulate comprise (1) a porous matrix of a water-insoluble, hydrophilic, normally solid, organic polymer bearing a plurality of pendant anionic moieties and (2) dispersed in said matrix, a water-insoluble inorganic compound capable of removing metal ions from an aqueous medium, said particles being permeable to the passage of the metal ions from the aqueous medium under conditions such that a substantial portion of said metal ions are removed from the aqueous medium and retained in the matrix when the particles are contacted with the aqueous medium.

2. The particulate of Claim 1 and further characterized in that the amount of water-insoluble compound in the particulate is sufficient to increase the capacity of the particulate to remove and retain the metal ions from the aqueous medium by at least 10 weight percent, as compared to the capacity of the polymer containing none of the water-insoluble compound.

3. The particulate of Claim 1 or 2 and further characterized in that the polymer is a cation--exchange resin and the water-insoluble compound is a salt of an acid and a metal similar to the metal ion being removed from the aqueous medium.

4. The particulate of Claim 1 and further characterized in that the cation-exchange resin is a sulfonated copolymer of styrene and divinylbenzene, the salt is a water-insoluble barium compound and the metal ion is divalent radium.

5. The particulate of Claim 4 and further characterized in that the cation-exchange resin is a macroporous resin.

6. A process for preparing an adsorptive resin for removing and retaining metal ions from an aqueous medium characterized by (1) contacting finely divided particles of a water-insoluble, hydrophilic polymer bearing pendant anionic moieties in the interior regions of the particles with an aqueous solution of a compound of a similar metal under conditions such that a salt of the metal and a desired portion of the anionic moieties in said interior regions are formed and (2) contacting the resulting metal salt form of the particles with a reactant under conditions such that (1) the reactant invades said interior regions and reacts with the similar metal to form a water-insoluble compound capable of removing the desired metal ion from an aqueous medium and (b) the resulting particles containing the water-insoluble compound are permeable to the the transport of metal ions into the interior regions of the particles.

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7. The process of Claim 6 characterized in that the polymer is a sulfonated copolymer of styrene and divinylbenzene, the water-soluble salt is barium hydroxide and the reactant is sulfuric acid having a concentration of 6 to 16 moles per liter.

8. A method for removing and retaining metal ion from an aqueous liquid which comprises contacting the particulate of Claim 1 with the aqueous medium under conditions such that the metal ions pass into the interior regions of the particles of the resin and are thereby removed from the aqueous liquid.

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Application number

EUROPEAN SEARCH REPORT

EP 82 10 6489

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	GB-A- 769 121 (AUXILLIAIRE DES CHEMINS DE FER) *Claims 1,2; example 3*	1,3,4, 8	G 21 F 9/12
A	GB-A-1 064 444 (RIESENHUBER) *Claim 1*	1,3	
A	GB-A- 796 441 (ATOMIC ENERGY OF CANADA)		

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

G 21 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	09-11-1982	NICOLAS H.J.F.

CATEGORY OF CITED DOCUMENTS

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