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(71) Applicant(s)
Lanxess Deutschland GmbH

(72) Inventor(s)
Halle, Olaf;Rossoni, Duilio;Podszun, Wolfgang;Klipper, Rheinhold;Hees, Bruno;Vesselle, Jean-Marc

(74) Agent / Attorney
Davies Collison Cave, 1 Nicholson Street, Melbourne, VIC, 3000

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- (71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): **BAYER CHEMICALS AG** [DE/DE]; 51368 Leverkusen (DE). **BAYER S.P.A.** [IT/IT]; Castella Postala 1243, I-20121 Milano (IT).
- (72) Erfinder; und
- (75) Erfinder/Anmelder (nur für US): **HALLE, Olaf** [DE/DE]; Wolfskaul 4, 51061 Köln (DE). **PODSZUN, Wolfgang** [DE/DE]; Roggendorfstrasse 55, 51061 Köln (DE). **HEES, Bruno** [DE/DE]; Zum Stadion 55, 40764 Langenfeld (DE). **KLIPPER, Rheinhold** [DE/DE]; Geilenkircherstr. 29, 50933 Köln (DE). **VESSELLE, Jean-Marc** [FR/DE]; Graf-Recke-Str. 21, 40237 Düsseldorf (DE). **ROSSONI, Duilio** [IT/IT]; Via Ombrianello 6, I-26013 Crema (IT).
- (74) Gemeinsamer Vertreter: **BAYER CHEMICALS AG**;
Law & Patents, Patents and Licensing, 51368 Leverkusen (DE).
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(54) Title: METHOD FOR THE PURIFICATION OF SULPHURIC ACIDS

(54) Bezeichnung: VERFAHREN ZUR REINIGUNG VON SCHWEFELSÄUREN

(57) Abstract: The invention relates to a method for the purification of sulphuric acids, in particular, metal-containing sulphuric acids, characterised in that monodisperse ion-exchangers with chelating functional groups are applied.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zur Reinigung von Schwefelsäuren, insbesondere von metallhaltigen Schwefelsäuren, dadurch gekennzeichnet, dass man monodisperse Ionenaustauscher mit chelatisierenden funktionellen Gruppen einsetzt.



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Method for the purification of sulphuric acids

The present invention relates to a process for purifying sulphuric acids, in particular metal-containing sulphuric acids, using monodisperse ion exchangers containing chelating functional groups.

5

The removal of impurities from sulphuric acids, particularly preferably from copper electrolytes containing sulphuric acids, has recently been becoming increasingly important. This process is employed, for example, before cathodic deposition of copper in electrolytic processes carried out in copper winning or refining processes. The task here is the removal

10 of metals which can occur in the oxidation state + III.

US-A 4 559 216 describes a process for removing antimony, bismuth or iron from copper electrolytes containing sulphuric acid using heterodisperse ion exchangers having specific chelating aminomethylenephosphonic acid groups. For example, Unicellex® UR 3300 is

15 mentioned there. US-A- 5 366 715 describes a process for removing antimony, bismuth or iron from copper electrolytes containing sulphuric acid by means of heterodisperse ion exchangers functionalized with amino-methylenephosphonic acid, preferably Duolite™ C-467, with a reduction of iron(III) to iron(II) firstly being carried out. In US-A 6 153 081, the abovementioned reduction of iron(III) to iron(II) is carried out using copper and

20 sodium chloride in sulphuric acid and after the ion exchanger has been laden with the impurities it is subjected to a specific elution in order to selectively isolate bismuth and then antimony. Use is once again made of heterodisperse chelating exchangers, preferably Epolas® MX-2 from Miyoshi Oil Co., Duolite™ C-467 or Unicellex® UR 3300.

25 All the processes suffer from poor kinetics, selectivity and stability of the ion exchangers used. In one or more aspects the present invention may advantageously provide a new process for purifying sulphuric acids, preferably for purifying metal-containing sulphuric acids, which makes it possible to remove impurities such as iron, antimony or bismuth selectively in copper winning or refining processes without the ion exchanger used

30 becoming exhausted too quickly. It has now surprisingly been found that the abovementioned properties can be improved when ion exchangers having a uniform particle size (hereinafter referred to as "monodisperse") are used.

The particle size of the ion exchangers used according to the invention is from 5 to 500 μm , preferably from 10 to 400 μm , particularly preferably from 20 to 300 μm . For the purposes of the present patent application, monodisperse ion exchangers are
5 ion exchangers which have a small width of the particle size distribution. Customary methods such as sieve analysis or image analysis are suitable for determining the mean particle size and the particle size distribution. The ratio of the 90% value $\varnothing(90)$ and the 10% value $\varnothing(10)$ of the volume distribution is employed as measure for the width of the particle size distribution of the ion exchangers used according to
10 the invention. The 90% value $\varnothing(90)$ is the diameter at which 90% of the particles have a smaller diameter. Correspondingly, 10% of the particles have a diameter smaller than the diameter of the 10% value $\varnothing(10)$. Monodisperse particle size distributions for the purposes of the invention are distributions such that $\varnothing(90)/\varnothing(10) \leq 1.50$, preferably $\varnothing(90)/\varnothing(10) \leq 1.25$, very particularly preferably
15 $\varnothing(90)/\varnothing(10) \leq 1.20$.

Monodisperse ion exchangers can be obtained by functionalization of monodisperse bead polymers. One possible way of preparing monodisperse bead polymers is to generate monodisperse monomer droplets by means of specific spraying techniques
20 and curing these by polymerization. The formation of a uniform droplet size can be effected by vibrational excitation, as described, for example, in EP-A 0 051 210. If the degree of monodispersity of the monomer droplets is to be retained in the polymerization, agglomeration and coalescence and also formation of new droplets has to be reliably prevented. A particularly effective method of preventing
25 agglomeration and coalescence and formation of new droplets is microencapsulation according to EP-A 0 046 535.

Various ways of preparing monodisperse ion exchangers having chelating functional groups (hereinafter referred to as "monodisperse chelating resins") are known.
30 US-A 4 444 961 describes a process for preparing monodisperse, macroporous chelating resins. Here, haloalkylated polymers are aminated and the aminated polymer is reacted with chloroacetic acid to form chelating resins of the iminodiacetic acid type. An alternative route is functionalization via a phthalimide stage, which is described in EP-A 1 078 690 for a monodisperse chelating resin. Both the
35 contents of US-A 4 444 961 and the contents of EP-A 1 078 690 are incorporated by

reference into the present description.

The present invention provides a process for purifying sulphuric acids, preferably metal-containing solutions containing sulphuric acid, particularly preferably copper electrolytes
5 containing sulphuric acid, characterized in that metals, particularly preferably metals which can be present as anions or cations, particularly preferably metals which can be present in the oxidation state +III, are treated with monodisperse ion exchangers having chelating functional groups, preferably of the aminomethylenephosphonic acid type or whose functionalization has been effected via the phthalimide stage.

10

In one aspect the present invention provides a process for removing copper from a metal containing sulphuric acid solution, characterized in that monodisperse chelating exchanges are used having a particle size from 5 to 500 μ m and a particle size distribution of $\frac{\text{D}^{\circ}(90)}{\text{D}^{\circ}(10)} \leq 1.50$ and the metal is antimony, bismuth, arsenic, cobalt, nickel,
15 molybdenum, iron or a combination thereof.

A further aspect of the invention provides a use of monodisperse chelating exchangers having a particle size from 5 to 500 μ m and particle size distribution of $\frac{\text{D}^{\circ}(90)}{\text{D}^{\circ}(10)} \leq 1.50$ for purifying copper electrolytes based on sulphuric acid containing additional metals
20 wherein the metals are antimony, bismuth, arsenic, cobalt, nickel, molybdenum, iron or a combination thereof.

According to the invention, contaminated sulphuric acids as are obtained in industrial production processes, preferably metal-containing sulphuric acids, particularly preferably
25 copper electrolytes which contain sulphuric acid and, in addition to copper, contain further metals such as iron, antimony or bismuth, can be worked up in this way and returned to the industrial production processes.

In the case of copper winning, there are various ways in which a metal-containing
30 sulphuric acid can be produced. In the first method, copper-containing milled ore is extracted with sulphuric acid and the pH is subsequently increased by addition of alkalis. Copper and other metals are extracted from this ore/sulphuric acid slurry by means of one

- 3a -

or more extractants. The extractant phase is separated off and the metals are reextracted into the sulphuric acid phase by addition of sulphuric acid. This sulphuric acid is then used as metal-containing sulphuric acid in the process of the invention.

- 5 In the production of sulphuric acid by this method for the purification process of the invention, it is also possible to use extractants or mixtures of sulphuric acid with a plurality of extractants. Suitable extractants are substances which form one or more phases in the presence of sulphuric acid and preferentially dissolve a metal, in the case of copper winning copper, in ionic or complexed form. Preferred extractants are aliphatic or
- 10 aromatic or mixed aliphatic and aromatic organic compounds having functional groups. Preferred functional groups are, for example, phosphate (e.g. in trialkyl phosphate), aldoxime, ketoxime, alcohol, ketone, β -diketone, ester and sulphonamide.

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In a further alternative embodiment, elemental copper contaminated with metals which can occur in the oxidation state +III is brought into solution in the presence of sulphuric acid by anodic oxidation in an electric field. Such sulphuric acid can also
5 be used as appropriate metal-containing sulphuric acid in the process of the invention.

The concentration of these sulphuric acids can vary within a wide range. The preferred sulphuric acid concentration for the process of the invention is 50-500 g/l,
10 particularly preferably 75-400 g/l, very particularly preferably 125-275 g/l.

The amounts of metals in the sulphuric acid to be used according to the invention, in particular the amount of copper and the amounts of other metals, can fluctuate within a wide range and are dependent on the quality of the ore and the extraction process.
15 In the case of copper winning, the preferred concentration of copper in the sulphuric acid is 5-100 g/l, particularly preferably 20-50 g/l, very particularly preferably 25-35 g/l.

In the process of the invention, preference is given to removing metals which can
20 occur in the oxidation state +III from the sulphuric acids. Preferred metals are one or more metals of the group consisting of antimony, bismuth, arsenic, cobalt, nickel, molybdenum and iron. Particularly preferred metals are one or more metals from the group consisting of antimony, bismuth and molybdenum, very particularly preferably antimony or bismuth. The preferred antimony concentration is 0-5 g/l, particularly
25 preferably 0-2 g/l, very particularly preferably 0.1-1 g/l. The preferred bismuth concentration is 0-5 g/l, particularly preferably 0-2 g/l, very particularly preferably 0.1-1 g/l.

The process of the invention can be carried out continuously or batchwise.
30 Preference is given to continuous processes. Here, the resin is employed in a column provided with perforated plates. Here, the speed at which the sulphuric acid to be purified travels through the column should be chosen so that a high volume flow passes through the column but elevated concentrations of the metals to be removed do not remain in the stream leaving the column. The preferred flow rate through the
35 column is 5-30 times the ion exchanger bed volume per hour (this unit is hereinafter

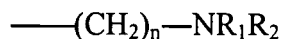
referred to as bed volume per hour (BV/h)), particularly preferably 10-20 BV/h.

As a result of the use of the ion-exchange resin according to the invention, the metals to be removed accumulate in the ion-exchange resin. These can be eluted by setting
5 conditions under which the chemical affinity of the metals to the ion-exchange resin is reduced. An effective method of eluting ion exchangers is treatment with mineral acids or organic acids, preferably in a concentration of 0.1-10 eq/l. Elution is usually carried out using 1-10 bed volumes (BV), preferably 2-5 BV. Preferred mineral acids are hydrochloric acid or sulphuric acid, while preferred organic acids are acetic acid,
10 formic acid or tartaric acid. Organic salts (e.g. tartrates) or inorganic salts (e.g. sodium chloride) can also be present during elution.

The sulphuric acid purified by means of the monodisperse chelating exchanger can finally be used directly in electrolytic processes for the production of elemental
15 copper by reduction of the cathode.

Functional groups in the monodisperse chelating exchangers used according to the invention can be all chelate-forming functional groups. Preference is given to functional groups of the type

20



where

R₁ is hydrogen or a CH₂-COOH or CH₂-P(O)(OH)₂ radical and

25 R₂ is a CH₂-COOH or CH₂-P(O)(OH)₂ radical and

n is an integer from 1 to 4.

Particular preference is given to functional groups of the type -(CH₂)_n-NR₁R₂

in which

R₁ is hydrogen or the radical CH₂P(O)(OH)₂,

30 R₂ is CH₂P(O)(OH)₂ and

n is 1, 2, 3 or 4.

Preference is likewise given to all anionic forms or salts of metals in the oxidation

states +I and +II which are formed by abstraction or replacement of the acidic hydrogen of the functional group.

5 As polymer base of the monodisperse chelating exchangers to be used according to the invention, various basic structures are known. It is customary to employ ion exchangers based on crosslinked vinylaromatic polymers and ion exchangers based on condensation products of hydroxyaromatics and formaldehyde. However, ion exchangers based on aliphatic polyamines, polyesters or natural products, e.g. cellulose or wood, are also known. According to the invention, preference is given to
10 monodisperse chelating exchangers based on crosslinked vinylaromatic polymers.

The monodisperse, crosslinked, vinylaromatic base polymer can be prepared by methods known from the literature. For example, such methods are described in US-A 4 444 961, EP-A 0 046 535, US-A 4 419 245, WO 93/12167.

15 A possible copolymer for the purposes of the present invention is, for example, a copolymer composed of a monovinylaromatic compound and a polyvinylaromatic compound.

20 As monovinylaromatic compounds, preference is given, for the purposes of the present invention, to monoethylenically unsaturated compounds such as styrene, vinyltoluene, ethylstyrene, α -methylstyrene, chlorostyrene, chloromethylstyrene, alkyl acrylates and alkyl methacrylates.

25 Particular preference is given to using styrene or mixtures of styrene with the abovementioned monomers.

Polyvinylaromatic compounds which are preferred for the purposes of the present invention are multifunctional ethylenically unsaturated compounds such as divinyl-
30 benzene, divinyltoluene, trivinylbenzene, divinyl-naphthalene, trivinyl-naphthalene, 1,7-octadiene, 1,5-hexadiene, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate or allyl methacrylate.

The polyvinylaromatic compounds are generally used in amounts of 1-20% by
35 weight, preferably 2-12% by weight, particularly preferably 4-10% by weight, based

on the monomer or its mixture with further monomers. The type of polyvinyl-aromatic compounds (crosslinkers) is selected with a view to the later use of the spherical polymers. Divinylbenzene is suitable in many cases. Commercial divinylbenzene grades which contain ethylvinylbenzene in addition to the isomers of
5 divinylbenzene are satisfactory for most applications.

In a preferred variant for preparing monodisperse chelating exchangers to be used according to the invention, microencapsulated monomer droplets are used as bead
10 polymers. The microencapsulation of the monomer droplets can be by means of the materials known for use as complex coacervates, in particular polyesters, natural and synthetic polyamides, polyurethanes, polyureas.

A particularly useful natural polyamide is, for example, gelatin. This is employed, in particular, as coacervate and complex coacervate. For the purposes of the invention,
15 gelatin-containing complex coacervates are, in particular, combinations of gelatin with synthetic polyelectrolytes. Suitable synthetic polyelectrolytes are copolymers containing built-in units of, for example, maleic acid, acrylic acid, methacrylic acid, acrylamide and methacrylamide. Particular preference is given to using acrylic acid and acrylamide. Gelatin-containing capsules can be cured by means of customary
20 curing agents such as formaldehyde or glutaraldehyde. The encapsulation of monomer droplets by means of gelatin, gelatin-containing coacervates and gelatin-containing complex coacervates is described in detail in EP-A 0 046 535. Methods of encapsulation using synthetic polymers are known. One well-suited method is, for example, phase interface condensation in which a reactive component (for example
25 an isocyanate or an acid chloride) dissolved in the monomer droplet is reacted with a second reactive component (for example an amine) dissolved in the aqueous phase.

The optionally microencapsulated monomer droplets may, if appropriate, contain an initiator or mixtures of initiators to trigger the polymerization. To prepare the
30 chelating exchanger used according to the invention, preference is given to using initiators preferred in the preparation of bead polymers, for example peroxy compounds such as dibenzoyl peroxide, dilauryl peroxide, bis(p-chlorobenzoyl) peroxide, dicyclohexyl peroxydicarbonate, tert-butyl peroctoate, tert-butyl peroxy-2-ethylhexanoate, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane or tert-amyl-
35 peroxy-2-ethylhexane, and also azo compounds such as 2,2'-azobis(isobutyronitrile)

or 2,2'-azobis(2-methylisobutyronitrile).

The initiators are generally employed in amounts of from 0.05 to 2.5% by weight, preferably from 0.1 to 1.5% by weight, based on the monomer mixture.

5

As further additives in the optionally microencapsulated monomer droplets, it is possible to use porogens in order to produce spherical bead polymers (starting material for the preparation of the monodisperse chelating exchanger) having a macroporous structure. Examples of suitable porogens are organic solvents which do not readily dissolve or swell the bead polymer formed. Examples which may be mentioned are hexane, octane, isooctane, isododecane, methyl ethyl ketone, butanol or octanol and their isomers.

The terms microporous or gel-like or macroporous are described in detail in the specialist literature.

The optionally microencapsulated monomer droplet can, if desired, also contain up to 30% by weight (based on the monomer) of crosslinked or uncrosslinked polymer. Preferred polymers are derived from the abovementioned monomers, particularly preferably from styrene.

The mean particle size of the optionally encapsulated monomer droplets necessary for preparing the bead polymer (starting material for the preparation of the monodisperse chelating exchangers) is 10-1000 μm , preferably 100-1000 μm .

25

The functionalization of the bead polymers to produce the desired monodisperse chelating exchanger used according to the invention can be carried out via haloalkylation of the crosslinked polymer and subsequent conversion into the desired functional group. Methods of haloalkylating polymers are known from US-A 4 444 961. A preferred haloalkylating agent is chloromethyl methyl ether.

The chloromethyl methyl ether can be used in unpurified form, in which case it can contain, for example, methylal or methanol as secondary components. The chloromethylation reaction is catalysed by addition of Lewis acids. Suitable catalysts are, for example, iron(III) chloride, zinc chloride, tin(IV) chloride and aluminium

35

chloride.

The general preparation of heterodisperse ion-exchange resins containing chelating groups is described, for example, in US-A 2 888 441, but can be applied to
5 monodisperse ion exchangers. In this method, the haloalkylated bead polymer is aminated and the aminated bead polymer is reacted with a suitable carboxyl-containing compound, e.g. chloroacetic acid. However, it is also possible to react the haloalkylated bead polymer directly with suitable amino acids such as aminodiacetic acid, glycine, 2-picolylamine or N-methyl-2-picolylamine.

10

In a preferred form, the functionalization of the bead polymer to the desired monodisperse chelating exchanger is carried out by direct amination. For this purpose, the amidomethylation reagent is prepared first. To achieve this, phthalimide or a phthalimide derivative, for example, is dissolved in a solvent and admixed with
15 formaldehyde or paraformaldehyde. A bis(phthalimido) ether is subsequently formed from this by elimination of water. The bead polymer is subsequently condensed with phthalimide derivatives. As catalyst, use is made here of oleum, sulphuric acid or sulphur trioxide.

20 The phthalic ester is split off to set the aminomethyl group free by treatment of the phthalimidomethylated crosslinked bead polymer with aqueous or alcoholic solutions of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide at temperatures of from 100 to 250°C, preferably 120-190°C. The concentration of the sodium hydroxide solution is in the range from 10 to 50% by weight, preferably from
25 20 to 40% by weight. This process makes it possible to produce aminoalkyl-containing crosslinked bead polymers having a degree of substitution of the aromatic rings of more than 1.

The ion exchangers to be used according to the invention are subsequently prepared
30 by reacting the aminated monodisperse, crosslinked, vinylaromatic base polymer in suspension with compounds which finally develop, as functional amine, chelating properties.

Preferred reagents are chloroacetic acid and its derivatives, formaldehyde in
35 combination with P-H-acidic (after modified Mannich reaction) compounds such as

phosphorous acid, monoalkylphosphorous esters or dialkylphosphorous esters.

Particular preference is given to using chloroacetic acid or formaldehyde in combination with P-H-acidic compounds such as phosphorous acid.

5

The monodisperse chelating exchangers to be used according to the invention preferably have a macroporous structure.

Examples

Example 1

5 **1a) Preparation of the monodisperse, macroporous bead polymer based on styrene, divinylbenzene and ethylstyrene**

3000 g of deionized water are placed in a 10 l glass reactor and a solution of 10 g of gelatin, 16 g of disodium hydrogenphosphate dodecahydrate and 0.73 g of resorcinol
10 in 320 g of deionized water is introduced and the mixture is mixed. The mixture is brought to 25°C. While stirring, a mixture of 3200 g of microencapsulated monomer droplets having a narrow particle size distribution and comprising 3.6% by weight of divinylbenzene and 0.9% by weight of ethylstyrene (used as commercial isomer mixture of divinylbenzene and ethylstyrene containing 80% of divinylbenzene),
15 0.5% by weight of dibenzoyl peroxide, 56.2% by weight of styrene and 38.8% by weight of isododecane (industrial isomer mixture having a high proportion of penta-methylheptane), with the microcapsule comprising a formaldehyde-cured complex coacervate of gelatin and a copolymer of acrylamide and acrylic acid, is subsequently introduced and 3200 g of aqueous phase having a pH of 12 are added. The mean
20 particle size of the monomer droplets is 460 µm.

The mixture is polymerized while stirring by increasing the temperature according to a temperature programme commencing at 25°C and ending at 95°C. The mixture is cooled, washed on a 32 µm sieve and subsequently dried at 80°C under reduced
25 pressure. This gives 1893 g of a spherical polymer having a mean particle size of 440 µm, a narrow particle size distribution and a smooth surface.

The polymer is chalky white in appearance and has a bulk density of about 370 g/l.

30 **1b) Preparation of the amidomethylated bead polymer**

1149 g of dichloroethane, 341 g of phthalimide and 238 g of a 29.8% strength by weight formaldehyde solution are placed in a reaction vessel at room temperature. The pH of the suspension is adjusted to 5.5 to 6 by means of sodium hydroxide
35 solution. The water is subsequently removed by distillation. 24.8 g of sulphuric acid

are then added. The water formed is removed by distillation. The mixture is cooled. At 30°C, 91 g of 65% strength by weight oleum and subsequently 424.8 g of monodisperse bead polymer prepared as described in process step 1a) are metered in. The suspension is heated to 70°C and stirred at this temperature for a further 6 hours.

- 5 The liquid phase is taken off, deionized water is added and residual amounts of dichloroethane are removed by distillation.

Yield of amidomethylated bead polymer: 1480 ml

- 10 Elemental analysis:

carbon: 80.7% by weight;

hydrogen: 5.6% by weight;

15

nitrogen: 3.9% by weight;

balance: oxygen.

- 20 **1c) Preparation of the aminomethylated bead polymer**

492 g of 50% strength by weight sodium hydroxide solution and 1006 ml of deionized water are added to 1460 ml of amidomethylated bead polymer at room temperature. The suspension is heated to 180°C and stirred at this temperature for
25 8 hours.

The bead polymer obtained is washed with deionized water.

The total yield is 1399 ml.

30

Elemental analysis: nitrogen 5.8% by weight

1d) Preparation of the ion exchanger containing aminomethylphosphonic acid groups

5 540 ml of the moist aminomethylated bead polymer from 1 c) are placed in a round-bottom flask and admixed with 281 ml of deionized water. While stirring, 209 g of dimethyl phosphite having a purity of 99% by weight are added dropwise over a period of 15 minutes and the mixture is subsequently stirred for another 30 minutes. 648 g of 98% strength sulphuric acid are then metered in uniformly over a period of
10 four hours. After this time, the mixture is heated to 100°C, 291 g of a 29.8% strength by weight formaldehyde solution is metered in at this temperature over a period of one hour and the mixture is stirred for a further six hours at reflux temperature.

The reaction mixture is cooled, poured onto a sieve and washed with deionized water
15 until the washings remain neutral. The resin is subsequently transferred to a glass column having a glass frit bottom and is converted into the sodium form by means of 3 bed volumes of 4% strength by weight sodium hydroxide solution which is introduced into the ion exchanger bed from the top. The ion exchanger is then washed with 5 bed volumes of deionized water. This gives 1060 ml of a moist ion
20 exchanger.

Elemental analysis:

nitrogen: 3.2% by weight
25

phosphorus: 10.0% by weight

Before use for the intended purpose, the ion exchanger is again transferred to the glass column and converted into the hydrogen form by means of 2 bed volumes of
30 10% strength by weight sulphuric acid which is introduced into the ion exchanger bed from the top. The ion exchanger is then washed with 5 bed volumes of deionized water and removed from the glass column again.

**1e) Preparation of a sulphuric acid composition to be purified by way of
35 example**

3 l of deionized water are placed in a 5 l glass beaker, 1000 g of 98% strength sulphuric acid are added and, while stirring, 3.28 g of antimony(III) chloride and 517.5 g of copper(II) sulphate pentahydrate are dissolved in the mixture. The mixture is subsequently made up to 5000 g with deionized water and cooled to room temperature.

This gives a sulphuric acid containing, as intended, 30 g/l of copper and 0.4 g/l of antimony.

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1f) Purification of the sulphuric acid composition from 1e) according to the invention

100 ml of the monodisperse ion exchanger from 1 d) are transferred to a glass column having a glass frit bottom (internal diameter = 22 mm). The sulphuric acid from 1 e) is passed through this glass column at a volume flow of 500 ml/h in such a way that a constant small volume of sulphuric acid is always present over the ion exchanger bed.

20 The sulphuric acid exiting the glass column is analysed and compared with the inflowing sulphuric acid from 1 e).

Inflowing sulphuric acid

25 Concentration of antimony: 0.4 g/l

Outflowing sulphuric acid after 10 BV

Concentration of antimony: 0.02 g/l

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Surprisingly, the reduction in the antimony content of the sulphuric acid to be purified by means of a monodisperse chelating exchanger is significantly better than when using the abovementioned heterodisperse ion exchangers known from the prior art.

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Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of

10 endeavour to which this specification relates.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for removing copper from a metal containing sulphuric acid solution, characterized in that monodisperse chelating exchanges are used having a particle size from 5 to 500 μ m and a particle size distribution of $\emptyset^{\circ}(90)/\emptyset^{\circ}(10) \leq 1.50$ and the metal is antimony, bismuth, arsenic, cobalt, nickel, molybdenum, iron or a combination thereof.
2. Process according to Claim 1, characterized in that the monodisperse chelating exchangers bear functional groups of the type $-(CH_2)_n-NR_1R_2$, where
- R_1 is hydrogen or a CH_2-COOH or $CH_2P(O)(OH)_2$ radical and
- R_2 is a CH_2COOH or $CH_2P(O)(OH)_2$ radical and
- n is an integer from 1 to 4.
3. Process according to Claim 2, characterized in that the monodisperse chelating exchangers have a macroporous structure.
4. Use of monodisperse chelating exchangers having a particle size from 5 to 500 μ m and particle size distribution of $\emptyset^{\circ}(90)/\emptyset^{\circ}(10) \leq 1.50$ for purifying copper electrolytes based on sulphuric acid containing additional metals wherein the metals are antimony, bismuth, arsenic, cobalt, nickel, molybdenum, iron or a combination thereof.
5. Process for winning elemental copper, characterized in that the copper is obtained by reduction at the cathode in electrolytic processes directly from the sulphuric acids purified according to Claim 1.
6. Use according to Claim 4, characterized in that the purification concerns the

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elements Sb and Bi.

7. Process according to Claim 1 or Claim 5 substantially as hereinbefore described with reference to any one of the Examples.
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8. Use according to Claim 4 substantially as hereinbefore described with reference to any one of the Examples.