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Señor

**SUPERINTENDENTE DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

E. S. D.

SUPERINDUSTRIA Y COMERCIO

Radicación: 04068028 00000001

Folios: 3

Fecha (R): 2005-09-28 14:57:37

Trámite: 002 PATENTES D 1 REGISTRO/ 538 PETICION

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

REF: Expediente No.:
Patente de Invención:

04-068.028
"PROCESO PARA LA PRODUCCIÓN
DE POLISULFATO FERRICO EN
SOLUCIÓN"
ALFREDO DEL VALLE LAZO

Titular:

**Publicada en la Gaceta de la Propiedad Industrial No. 554 de
29 de julio de 2.005**

SOLICITUD DE EXAMEN DE PATENTABILIDAD

HUMBERTO RUBIO CAMACHO, mayor de edad, domiciliado en Bogotá, D.C., identificado con la cédula de ciudadanía número 17.192.062 de Bogotá, abogado Titulado con Tarjeta Profesional No. 50.007 del Consejo Superior de la Judicatura, actuando en carácter de APODERADO del Señor ALFREDO DEL VALLE LAZO; domiciliado en Comandante Chacón No. 6365, Cerro Navia, Santiago, Chile; respetuosamente solicito a esa Dependencia:

- 1.- De conformidad con lo establecido en el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina y estando dentro del termino legal de seis (6) meses contados desde la fecha de publicación en la Gaceta No. 554 de 29 de julio de 2.005, de la solicitud de la patente de la referencia, solicito se sirvan proceder a efectuar el examen de patentabilidad de la Invención.
- 2.- Para que la presente petición sea viable, estoy anexando los siguientes documentos:
 - 2.1. Recibos de pago Nos. 04-82,329 de 19 de octubre de 2.004 y 05-810 de 05 de enero de 2.005; para un valor total de \$ 371.000.00, de acuerdo con la Resolución No. 31980 de 24 de diciembre de 2.004.
- 3.- Por lo anterior solicito se continúe con el trámite correspondiente.

Del Señor Superintendente,



HUMBERTO RUBIO CAMACHO

C.C. 17.192.062 de Bogotá

T.P. 50.007 Consejo Superior
de la Judicatura.

COD. 4134

04/1771-01/pi
cpfm.-

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PARA USO EXCLUSIVO DE
HUMBERTO RUBIO & CIA. LTDA

**SOLICITUD DE EXAMEN DE
PATENTABILIDAD
PATENTE DE INVENCIÓN: PROCESO PARA
LA PRODUCCIÓN DE POLISULFATO
FÉRICO EN SOLUCIÓN**

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 04 - 82,329
FECHA : OCTUBRE 19 DE 2004

SUPERINDUSTRIA Y COMERCIO
Radicación : 04066028 00000001 Folios: 3
Fecha (AMB) : 2005-09-28 14:57:37
Trámite : 002 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
HUMBERTO RUBIO ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	33700253	19/10/2004	5,447,800.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		112 PTC CAP-I EXAMEN DE PATENTIBILIDAD	353,000.00
		TOTAL :	353,000.00

SON: TRESCIENTOS CINCUENTA Y TRES MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

SOLICITUD DE EXAMEN DE
PATENTABILIDAD
PATENTE DE INVENCION: PROCESO PARA
LA PRODUCCION DE POLISULFATO
FERRICO EN SOLUCION

CERTIFICACION DE EXCEDENTE : 05 - 810
FECHA : ENERO 5 DE 2005

SUPERINDUSTRIA Y COMERCIO
Radicacion : 04060026 00000001 Folios: 3
Fecha (AMD): 2005-09-28 14:57:37
Tramite : 002 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
HUMBERTO RUBIO CANACHO	CONSIGNACION	BANCO POPULAR	050-00110-6	34724255	04/01/2005	1,096,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	
		99 OTROS SERVICIOS ADMINISTRATIVOS	18,000.00
		TOTAL :	\$ 18,000.00

SON: DIEZ Y OCHO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

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DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 04-68028

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 554, DE

FECHA 29 DE JULIO DE 2005, EL TERMINO HABIL SEÑALADO POR LA LEY

EXPIRA EL 25 DE OCTUBRE DE 2005.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 30 de Noviembre de 2006

Doctor

HUMBERTO RUBIO CAMACHO

Representante **ALFREDO DEL VALLE LAZO**

ASUNTO

Radicación No.	04-68028
Trámite	002
Evento	001
Actuación	430
Oficio	014260
Folios	020

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 9 a 23 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 18 reivindicaciones en los folios 24 a 27 de la solicitud en estudio.
- c) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 16 de julio de 2004, y en el momento de la radicación **SI** se reclamo prioridad de la primera solicitud presentada en Chile 1515-2003

2) Objeto de la invención

- a) Las reivindicaciones 1 a 18 de la solicitud en estudio se refieren a un proceso para obtener polisulfato férrico en solución a partir de mineral de magnetita refinada y concentrada, útil como coagulante en los procesos de tratamiento de aguas domiciliarias y/o industriales, **CARACTERIZADO** porque comprende: a. Mezclar en un reactor sellado agua o un polisulfato férrico/ferroso de baja concentración diluido, un electrolito frío formado por ácido sulfúrico y agua y mineral de magnetita en exceso; b. Agitar la solución formada en el paso a) al interior del reactor durante todo el proceso; c. Cerrar el reactor y adicionar ácido sulfúrico industrial faltante; d. Obtener una solución con alrededor de 220 a 280 g de Hierro por litro de solución, acidez libre de 0%, basicidad entre 2% y un 12,5% y pH entre alrededor de 0,2 a 1,0; e. Filtrar la solución obtenida en paso d) en caliente a aproximadamente entre unos 80° y 100° C; f. Aplicar un oxidante a la solución filtrada por la parte inferior de un reactor abierto a presión atmosférica; y g. Obtener un polisulfato férrico en solución con concentraciones de ión férrico de al menos 12,5%, ión ferroso menor a 4 g/l, acidez libre igual a cero, basicidad entre 7% y 22 % y pH entre alrededor de 0,5 a 1,8.

- b) El anterior procedimiento busca obtener un polisulfato férrico en solución.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 01 G 49/14

3) Claridad de la Solicitud

El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro toda vez que:

- a) La redacción del punto 1. a. no es la mejor toda vez que genera confusión. Primero, porque no son claras las proporciones a emplear de los componentes. Segundo, nótese que al leer de corrido dicho punto existe una muy buena cantidad de conjunciones empleadas, lo que dificulta su correcta lectura. Por lo mismo se sugiere que se diga algo como "mezclar en un reactor: un componente A constituido por agua o un polisulfato férrico/ferroso de baja concentración, un componente B formado por un electrolito frío formado por ácido sulfúrico y agua y un componente C el cual es mineral de magnetita en exceso...".
- b) El punto 1. c. no es claro toda vez que nunca se dice que al inicio no se agrega todo el ácido sulfúrico, o, que es necesario más ácido sulfúrico en esta etapa 1. c. Un técnico no podría entender cuanto es el "ácido sulfúrico faltante"
- c) El punto 1. f. no es claro toda vez que no se sugiere que el filtrado se pasa a un reactor abierto y que allí se le agrega el oxidante. Mejorar la redacción.
- d) La última parte de la reivindicación 15 (se obtiene de un proceso que no requiere...etc.) caracteriza dicha reivindicación por el resultado, mas no por la forma en que se llegó a ese resultado. Esto es inadmisibles. Las reivindicaciones deben caracterizar un producto por la forma o constitución del mismo, las partes que lo componen y todo lo que permita establecer de cómo se llegó a ese resultado. No se aceptan reivindicaciones que caractericen resultados. Se debe eliminar dicha parte o colocarla dependiente de las reivindicaciones anteriores.
- i) No se aceptan frases tales como 'alrededor de...' o "aproximadamente".

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 01 G 49/14 y las más cercanas a ellas, se encontró que antes del 29 de julio de 2003 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con procesos para la producción de polisulfato férrico en solución.

De acuerdo con o establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	WO 95/23765	Preparations and uses of polyferric sulphate	1995.09.08
D2	EP 0 885 846	Method for preparing ferric polysulphate solutions	1998.12.23

5) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación del Nivel Inventivo

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

La presente solicitud relaciona un proceso que comprende los siguientes pasos:

- * Mezclar en un reactor A) agua o un polisulfato férrico/ferroso de baja concentración diluido, B) un electrolito frío formado por ácido sulfúrico y agua y C) mineral de magnetita en exceso;
- * Agitar la solución formada durante todo el proceso;
- * Cerrar el reactor y adicionar más ácido sulfúrico industrial
- * Obtener una solución
- * Filtrar la solución obtenida en caliente entre 80° y 100° C;
- * Aplicar un oxidante a la solución filtrada
- * Obtener un polisulfato férrico en solución.

D1 (WO95/95/23765) relaciona un proceso que consta de los siguientes pasos:

- * Se inicia con solución acuosa acida que comprende sulfato ferroso que se oxida a sulfato férrico. Se emplea un agente de oxidación como el de la presente solicitud. También aquí se incorpora ácido sulfúrico. El pH es como el de la presente solicitud.
- * Dicho sulfato férrico se hidroliza parcialmente. Las temperaturas son como las de la presente solicitud.
- * Se polimeriza.

Los agentes oxidantes son los mismos empleados por la presente solicitud. Las temperaturas y pH's son como los de la presente solicitud. En general D1 contempla los últimos pasos de la presente solicitud.

D2 relaciona un proceso en el que se colocan desperdicios que contienen hierro y se hacen reaccionar con ácido sulfúrico. Las relaciones entre reactantes se controlan durante el proceso. Podría decirse que corresponde a las primeras etapas del proceso objeto de la presente solicitud.

Por consiguiente, la presente solicitud podría hallarse uniendo estos dos documentos. Un técnico medio podría considerar iniciar con el procedimiento propuesto por D2 y terminarlo como lo que relaciona D1. de aquí que la presente solicitud podría carecer del nivel inventivo para que se le conceda el privilegio solicitado.

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

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Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	WO 95/23765	1 -18	Nivel inventivo
D2	EP 0 885 846	1 - 18	Nivel inventivo

6) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única Nº 10 de 2001


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha

11 DIC. 2006

Concepto Técnico Nº	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
1879	202003	

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

[illegible]

100 THE PREPARATION AND USE OF POLYMERIC SUBSTRATE

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A process for preparing a polyamide films of fibrillar regions wherein an acidic aqueous solution comprising fibrous segments is coadded to form fibrillar segments, and addition of an oxidation step at suitable pressure and in the absence of oxidizing catalyst yielding at least one oxidized segment; said fibrillar segments subsequently being added by addition to said solution of at least one compound which reacts with the fibrillar segments being held in contact with said base at the temperature selected for a time sufficient for polymerization of the at least partially hydrolyzed fibrillar segments. The polyamide film (PFA) obtained by subsequent treatment of such a process can be used as a component in a wide variety of applications.

As stated, it may sometimes be desirable to produce polymers with improved performance compared to conventional polymers and techniques are known.

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PREPARATIONS AND USES OF POLYFERRIC SULPHATE

Chemical coagulants for drinking water, to purify and/or decolourise municipal water supplies for human consumption are known and include iron and aluminium-based inorganic coagulants.

Polyferric sulphate, PFS, is one known form of coagulant which has also been used to treat municipal and industrial waste waters to help remove, by flocculation, suspended organic waste matter. There is currently considerable interest in the more widespread application of PFS as coagulants. Because of its relative efficiency, PFS may need less chemical addition, it can have a greater removal capacity and may reduce the volumes of waste concentrates that require disposal or further treatments.

PFS is a known chemical and there are several patents describing methods for its preparation.

The present invention is concerned with methods for preparing polymeric forms of ferric sulphate, of which PFS is an example.

Essentially, the chemical can be prepared according to this invention by oxidising ferrous sulphate to ferric sulphate, and then carrying out a controlled, partial hydrolysis of the ferric sulphate to produce a heterogeneous mixture of iron (III) hydrolysis species, $[\text{Fe}(\text{OH})_x]^{(3-x)+}$, and polynuclear complexes of iron (III), $(\text{Fe}_m(\text{OH})_x)_n^{(3m-x)n+}$. The functions of these species are to provide both colloid charge neutralization and polymer bridging between floc particles, leading in practice to a

greater coagulating (and therefore, treatment) performance.

According to this invention there is provided a process for preparing a polymeric form of ferric sulphate wherein an acidic aqueous solution comprising ferrous sulphate is oxidised to form ferric sulphate in said solution in an oxidation stage at ambient pressure and in the absence of oxidation catalyst preferably using at least one oxidising agent from the following: ozone, nitric acid, peroxide, perchlorate and persulphate,

said ferric sulphate subsequently being at least partially hydrolysed by addition to said solution of at least one base, the ferric sulphate being kept in contact with said base at the temperature selected for a time sufficient for polymerisation of the at least partially hydrolysed ferric sulphate.

The ferrous sulphate solution may be rendered acidic by addition of e.g. sulphuric acid. This may usefully increase the level of sulphate ions in solution, without adding unwanted ionic species. The pH of the starting solution is preferably less than 2.0, more preferably in the range 0.8 to 1.5.

Preferably the oxidation stage is a one-step oxidation stage. Preferred oxidising agents include peroxide and nitric acid. It is possible to use strong concentrated or even fuming nitric acid.

Accordingly the concentration of the nitric acid used in the oxidation stage is preferably at least 50% by volume, more preferably at least 70% by volume although nitric acid as concentrated as 90% by volume can be used.

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It is also preferred to use peroxide as an oxidising agent and more preferably hydrogen peroxide. The strength of the hydrogen peroxide used, as with the option of nitric acid mentioned above, may be dictated by the economics of the cost of raw materials, oxidation temperature and oxidation time.

Thus a stronger oxidising agent will most likely allow a shorter oxidation time and/or a lower oxidation reaction temperature. With hydrogen peroxide at very strong concentration, perhaps of the order 30 volumes, it may even be possible to effect the oxidation stage at ambient temperatures, for example at a temperature in the range of 15° to 25°C. Oxidation temperatures when using hydrogen peroxide may be 70°C or lower, such as 60°C or lower, preferably no higher than 50°C.

Oxidation temperatures when using nitric acid as the oxidising agent, may be 110°C or lower, such as 90°C or lower, preferably no higher than 70°C (which temperature may be possible when using the very concentrated, fuming nitric acid having a strength of at least 90%).

The oxidation time for a preferred one-step oxidation stage may be up to 3 hours, for example up to 2 hours, more preferably 1.75 to 1 hours. The oxidation time, as with the oxidation temperature, may depend upon the nature and strength of the oxidising agent used and the molar ratio of oxidant : iron [Fe^{2+}].

It is preferred to carry out the oxidation such that there is a near-complete oxidation of ferrous [Fe^{2+}] ions to ferric [Fe^{3+}] ions. In consequence it is preferable

for the concentration of ferrous ions in the solution after the oxidation step to be less than 2.5% ($\text{Fe}^{2+}/\text{Fe}^{3+}$), more preferably less than 1.25% ($\text{Fe}^{2+}/\text{Fe}^{3+}$), most preferably less than 0.25% ($\text{Fe}^{2+}/\text{Fe}^{3+}$).

The molar ratio of oxidant : ferrous ions in the solution, for the oxidation stage may depend upon economics and the desire to bring about the aforementioned near-complete oxidation of ferrous ions in aqueous solution, to ferric ions in the same solution. The molar ratio may also be influenced by the choice of oxidising agent and its relative strength, the oxidation temperature required or otherwise selected and the oxidation time necessary for this near-complete oxidation.

For example, when using nitric acid as the oxidising agent at say 90°C, at a concentration of 70%, the preferred molar ratio of oxidant : ferrous ions present in the aqueous solution is no higher than 2:1, more preferably no higher than 1.5:1, most preferably about 1.13:1.

When using hydrogen peroxide as the oxidising agent at say 50°C at a strength of 30 vols, then the preferred molar ratio of oxidant : ferrous ions present in the aqueous solution is no higher than 3:1 preferably no higher than 2:1 most preferably about 1.81:1. These most preferred ratios have been found to achieve a near-complete oxidation of ferrous ions to ferric ions, i.e. $<0.5\text{g}[\text{Fe}^{2+}]$ per litre after oxidation, when the oxidation has been allowed to proceed for about 1½ hours.

We have also used this concentrated form of hydrogen peroxide (30 vols) in the oxidation stage, with a

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larger molar excess of oxidant : ferrous ions, at lower temperatures, even at ambient temperatures of about 20°C. For example a molar ratio of 2.9:1 oxidant : ferrous ions led to near-complete oxidation even in the absence of oxidation catalyst and at ambient (atmospheric) levels of pressure. Thus additional heat energy input for the oxidation may be avoided.

In the secondary stage of at least partial hydrolysis, it is possible simply to add one or more bases to the ferric sulphate which has been formed in aqueous solution. The base can be strong or weak inorganic bases such as a hydroxide or bicarbonate of an alkali metal. In particular sodium hydroxide or sodium bicarbonate can be used. The hydrolysis stage can be likened to an 'aging' step during which iron (III) hydrolysis species, $[\text{Fe}(\text{OH})_x]^{(3-x)+}$ and polynuclear complexes of iron (III), $[\text{Fe}_n(\text{OH})_x]^{(3n-x)n+}$ form as a polymeric form of ferric sulphate, often referred to in the technical field as polyferric sulphate (PFS).

The hydrolysis stage is most preferably carried out immediately after a one-step oxidation process, by simple addition of base to the ferric ions which have been formed in the acidic, aqueous solution. It has not been found necessary to remove or even otherwise purify the ferric sulphate formed after the oxidation stage.

The amount of base added is preferably such as to provide an $[\text{OH}]^- : [\text{Fe}]^{3+}$ molar ratio in the finished product obtained by the process, the polymeric form of ferric sulphate, of at least 0.1, preferably at least 0.2,

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more preferably 0.25 - 0.45:1.0. We have found that an actual ratio of 0.3:1 of $[\text{OH}]^- : [\text{Fe}]^{3+}$ in the final product gives a desirable optimum in terms of performance, costs and stability.

The amount of iron in the final polymeric form of ferric sulphate produced by the method can be for example, up to 30g.l^{-1} of iron, preferably up to 40g.l^{-1} of iron, even more preferably up to 200g.l^{-1} of iron and most preferably upto 350g.l^{-1} of iron.

Elevated temperature may be necessary for the hydrolysis/polymerisation to proceed to a satisfactory $[\text{OH}]^- : [\text{Fe}]^{3+}$ ratio, for example a temperature of at least 30°C, preferably at least 40°C more preferably 45°C or higher, such as 50°C. Moreover the ferric sulphate can be kept in contact with the base for a time sufficient to obtain the aforementioned ratios of hydroxyl : ferric ions in the final polymeric product. Up to 3 hours may be needed at 50°C, preferably at least 2 hours.

The polyferric sulphate (PFS) obtained is usually in the form of a liquid solution which may not require separation or purification prior to use.

In use the polymeric form of ferric sulphate obtained, hereinafter also referred to for convenience as 'polyferric sulphate' and abbreviated as PFS can be used as a coagulant or flocculant to help purify and/or decolourise water for drinking water supplies and/or to reduce pollutants be they organic or inorganic, nitrogen- or phosphorus-containing such pollutants in municipal and/or industrial wastewaters.

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The PFS obtained by processes according to the invention can be more economical in manufacture and/or confer better performance than PFS obtained by other commercially established procedures.

EXAMPLES 1 and 2 - PREPARATION

Example 1

The example described as follows is for the preparation of 500mL solutions of PFS with a Fe(III) concentration of 40 g/L, using nitric acid as an oxidant.

Prescription:

1. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (100%)	100g
2. H_2SO_4 (98%)	8.2 mL
3. HNO_3 (70%)	18.0 mL
4. Water	214.5 mL
5. NaHCO_3 (0.5N)	214.0 mL

Preparation procedure:

The ferrous sulphate, sulphuric acid and the water in the prescribed amounts were added to a one litre reactor with a speed controlled mixer. The reaction temperature was controlled by an electromantle. Then, the temperature of the mixed solutions was raised to 60 (± 0.2) °C accompanied by vigorous stirring. Nitric acid was added to the mixed solutions gently. After the addition of the nitric acid, the reaction temperature was raised to and kept at 90 (± 0.2) °C with continuing vigorous stirring, until more than 99% of ferrous iron has been oxidized to ferric iron (after approximately 1.5 to 2.0 hours). The residual concentrations of ferrous iron were detected by the 1, 10 - phenanthrene calorimetric method. The reaction temperature

was then reduced to and kept at 50 (± 0.2) °C. The sodium bicarbonate solution was added into the reaction solutions, and the addition rate was controlled to allow that all NaHCO_3 solution was added within a 30 minute period. Finally, the reaction solutions were maintained at a temperature of 50 (± 0.2) °C for another 1.5 hour period of aging. The PFS solution is thus prepared and, after cooling to room temperature is ready for use.

Properties of the prepared PFS:

$[\text{Fe(III)}] = 40 \text{ g/L}$, $[\text{Fe(II)}] \leq 0.2 \text{ g/L}$, OH/Fe (molar ratio) = 0.3, $\text{pH} = 0.9 - 1.1$,

Average electrophoresis mobility = $6 \pm 0.2 \mu\text{m cm/V s}$,

Size distribution of the molecular species in the PFS solution are:

low MW species ($< 0.5\text{K}$) = 20.0% (by weight of Fe),

medium MW species (0.5 - 10K) = 70.0% (by weight of Fe),

large MW species ($> 10\text{K}$) = 10.0% (by weight of Fe).

Stability:

The PFS solutions prepared by this method are stable over at least a 6 month stored period.

Example 2

The example described as follows is for the preparation of 500 mL solutions of PFS with a Fe(III) concentration of 40 g/L, using hydrogen peroxide as an oxidant.

Prescription:

1. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (100%)	100 g
2. H_2SO_4 (98%)	8.2 mL
3. H_2O_2 (30%)	20.0 mL
4. Water	212.5 mL
5. NaHCO_3 (0.5N)	214.0 mL

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Preparation procedure:

The ferrous sulphate, sulphuric acid and the water in the prescribed amounts were added to the one litre reactor, and the reaction temperature was controlled by an electromantle. Both the reactor and the electromantle were the same as used in the Example 1. The temperature of the mixed solutions was then raised to 40 (± 0.2)°C accompanied by vigorous stirring. H_2O_2 was added to the reaction solutions gently. After the addition of the hydrogen peroxide, the reaction temperature was raised to and kept at 50 (± 0.2)°C, and the oxidation process continued, until more than 99% of ferrous iron has been oxidized to ferric iron (after approximately 1.5 to 2.0 hours). The residual concentrations of ferrous iron were detected by the same method as described in the Example 1. The reaction temperature was kept at 50 (± 0.2)°C to carry out the aging process. The sodium bicarbonate solution was added into the reaction solutions, and the addition rate was controlled to allow that all $NaHCO_3$ solution was added within a 30 minute period. Finally, the reaction solutions were maintained at a temperature of 50 (± 0.2)°C for another 1.5 hour period of aging. The PFS solution is thus prepared and, after cooling to room temperature, is ready for use.

Properties of the prepared PFS:

$[Fe(III)] = 40 \text{ g/L}$, $[Fe(II)] \leq 0.2 \text{ g/L}$, OH/Fe (molar ratio) = 0.3, $pH = 1.0 - 1.1$,

Average electrophoresis mobility = $6 \pm 0.2 \mu\text{m cm} / \text{V s}$.

Size distribution of the molecular species in the PFS solutions are:

low MW species ($< 0.5K$) = 19.5% (by weight of Fe),

medium MW species (0.5 - 10K) = 69.0% (by weight of Fe),

higher MW species ($> 10K$) = 11.5% (by weight of Fe).

Stability:

The PFS solutions prepared by this method are stable over at least a 6 month stored period.

EXAMPLES 3 to 8

PFS solutions prepared by the methods described in the Examples 1 and 2 have been used as a coagulant for the treatment of algal-laden and upland coloured surface waters in laboratory test and pilot-plant scale experiments. For the laboratory jar test experiments, a six-beaker jar test apparatus was used with each beaker containing either 300 mL of real or model algal waters, or 500 mL of simulated coloured waters. The fast mixing time was 3 min at a paddle speed of 300 rpm, the flocculation period was 25 min at a paddle speed of 35 rpm, and the sedimentation period was 1 hour. Supernatant samples after settling were withdrawn for analysis of algal cells, turbidity, UV absorbance, DOC, colour, residuals of Fe, Mn and Al. The coagulation pH required was achieved by prior addition of either HCl or NaOH, and the solution pH was checked during the mixing and flocculation periods. To evaluate the coagulation performance at lower water temperatures (4°C), a special constant temperature bath was used with the jar test beakers. The low temperature of 4°C (± 0.2) was maintained throughout the whole coagulation process and the one hour settling period.

Pilot-plant experiments were undertaken which comprised the processes of pre-ozonation, coagulation, flocculation, dissolved-air flotation (DAF), sand

filtration, intermediate ozonation and either GAC or BAC. In the test period of about four weeks, the pilot plant was operated under the conditions of with and without application of ozone, with coagulants of either PFS or ferric sulphate (FS) for three doses (1,3,5 mg/L as Fe), and at a constant pH of 7.5 Raw water flow rate was 2 m³/hr. The pre-ozone dose and the contact time were 1.0 mg/L and 7.0 min, respectively; and the intermediate ozone dose was set to achieve a residual O₃ concentration of 0.25 mg/L after a contact time of 8.0 min. A separate set of samples was analysed to identify the kinds of algal species and to measure the total algal concentrations before and after treatment.

Table 1 presents example 3 using PFS and other comparative results (FS = ferric sulphate, AS = aluminium sulphate) for the treatment of two algal model waters in laboratory tests with the coagulants PFS, FS and AS at 18°C and at pH 7.5, for a given dose of 0.2 mM as Fe or Al. It can be seen that the coagulation performance of PFS in removing algae, turbidity, DOC, etc. was clearly superior to the other two conventional coagulants.

Table 2 summarises results with PFS (Example 4), FS and AS (both comparative) for the treatment of coloured waters at 18 and 4°C. It can be seen from Table 2. that under the optimum coagulation conditions at 18°C, the removal efficiency achieved by the three coagulants was close. However, the required PFS dose was the lowest (0.107 mM as Fe), compared to FS (0.143 mM as Fe), and AS (0.185 mM as Al), to achieve similar removal percentages. In

addition, as shown in Table 2, the coagulation performance of PFS did not appear to be influenced significantly by low water temperatures. For AS and FS, however, low water temperature appeared to have an adverse effect on the removals of UV-Abs and DOC; but the removals of colour were slightly reduced. Residual concentrations of FS and AS were slightly increased at low water temperatures.

Tables 3A and 3B show results from the pilot-plant experiments concerning the raw water qualities and removal efficiencies by DAF (Table 3 A) and by DAF and sand filters (Table 3B). PFS (Examples 5 to 8) displayed a much greater treatment performance in removing algae, turbidity, colour, TOC and UV-absorbance (254 nm). The removal percentages achieved by PFS at a dose of 3 mg/L were either similar or even superior to those achieved by FS at 5 mg/L, indicating that coagulant dosing costs may be reduced for the same treated water quality.

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Table 1. Comparison of the treatment performance of PFS, FS and AS at 18°C (Algal model waters)

	Coagulants		Total cell removal%		DOC removal%		Turbidity removal%		UV-Abs (254nm) removal%		Vis-Abs (420nm) removal%		Colloid (floc) charge ^a	
	X ^a	Y ^a	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
Example 3	PFS		96	86	61	45	88	79	50	48	54	48	65	20
	FS		80	61	33	24	69	60	40	36.5	45	36.5	28	-8
	AS		90	70	52	32	84	72	45	40	54	40	30	0

^a The unit is (mg/L) 10⁻⁴.

Coagulant dose for X and Y is 0.20 mM as Al³⁺ or Fe³⁺.

^a X - The water quality characteristics of *Asterionella* model waters:
Total cell conc. = 4.8 10⁶ cells mL⁻¹,
DOC = 2.5 ppm, UV-Abs (254 nm) = 9.6 m⁻¹,
pH = 8.3, Turbidity = 4 NTU,
Colloid charge = - 92 meq L⁻¹ 10⁻⁴.

^a Y - The water quality characteristics of synthetic algal waters (*Asterionella* "model" water + 2mg/L humic substances):
Total cell conc. = 5.0 10⁶ cells mL⁻¹,
DOC = 4.8 ppm, UV-Abs (254 nm) = 21.0 m⁻¹,
pH = 7.92, Turbidity = 4.5 NTU,
Colloid charge = - 115 meq L⁻¹ 10⁻⁴.

Table 2. Comparison of the treatment performance of PFS, FS and AS at 18°C and 4°C (Coloured waters)

Coagulant	Dose ^a (mg/L as Fe or Al)	pH ^a	Colour (420nm) R %		UV-Abs (254 nm) R %		DOC R %		Residual Fe (mg/L)		Residual Al (mg/L)		
			18°C	4°C	18°C	4°C	18°C	4°C	18°C	4°C	18°C	4°C	
			18°C	4°C	18°C	4°C	18°C	4°C	18°C	4°C	18°C	4°C	
Example 4	PFS	0.107	4	92.0	91.3	83.2	82.2	80.3	78.8	0.09	0.098		
	FS	0.143	4	91.1	89.5	84.8	80.5	80.2	76.7	0.165	0.180		
	AS	0.185	5	92.0	91.4	82.5	75.7	75.4	68.2			0.064	0.074
	Raw water	—	8.1	5.82 m ⁻¹		38.8 m ⁻¹		8.2 mg/L		0.05 mg/L		0.14 mg/L	

^a The coagulation pH and coagulant dosages were selected in terms of the optimal pH and minimum dose required to achieve >90% colour removal, >80% UV removal and >75% DOC removal at 18°C.

Table 3A Comparison of coagulation efficiency of PFS and FS in the pilot-plant experiments (by DAF.)

Running conditions	UV (254 nm) (m ⁻¹ h)		TOC (mg/L)		Colour (400 nm) (m ⁻¹ h)		Turbidity (NTU)		
	Raw water	R %	Raw water	R %	Raw water	R %	Raw water	R %	
Example 5	FS, 3 mg/L, no O ₃	11.0	13.64	6.17	10.8	12.0	36.67	2.5	48.0
	PFS, 3 mg/L, no O ₃	11.5	26.10	6.38	21.0	13.3	51.43	2.6	67.5
	FS, 5 mg/L, no O ₃	12.0	20.83	6.18	17.40	11.4	40.0	2.6	41.6
Example 6	FS, 5 mg/L, no O ₃	12.5	28.0	5.54	22.6	12.54	48.68	2.5	62.5

^a R % = Percentage removal.

Table 3B Comparison of coagulation efficiency of PFS and FS in the pilot-plant experiments. (by DAF and sand filters.)

Running conditions	UV (254 nm) (m ⁻¹ h)		TOC (mg/L)		Colour (400 nm) (m ⁻¹ h)		Turbidity (NTU)		Algae (cells/mL)		
	Raw water	R %	Raw water	R %	Raw water	R %	Raw water	R %	Raw water	R %	
Example 7	FS, 3 mg/L, no O ₃	11.0	18.18	6.17	21.90	12.0	39.83	2.5	64.8	79200	59.16
	PFS, 3 mg/L, no O ₃	11.5	30.43	6.38	24.76	13.3	53.23	2.6	73.0	249200	96.28
	FS, 5 mg/L, no O ₃	12.0	25.0	6.18	21.20	11.4	50.0	2.6	61.5	80000	54.57
Example 8	PFS, 5 mg/L, no O ₃	12.5	36.0	5.54	26.68	12.54	55.82	2.5	69.2	208325	70.14

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CLAIMS

1. A process for preparing a polymeric form of ferric sulphate wherein an acidic aqueous solution comprising ferrous sulphate is oxidised to form ferric sulphate in said solution in an oxidation stage at ambient pressure and in the absence of oxidation catalyst using at least one oxidising agent, said ferric sulphate subsequently being at least partially hydrolysed by addition to said solution of at least one base, the ferric sulphate being kept in contact with said base at the temperature selected for a time sufficient for polymerisation of the at least partially hydrolysed ferric sulphate.

2. A process as claimed in claim 1 wherein the oxidising agent comprises one or more of the following:

ozone, nitric acid, peroxide, perchlorate and persulphate.

3. A process as claimed in claim 1 or 2, wherein the aqueous solution comprising ferrous sulphate further comprises sulphuric acid.

4. A process as claimed in any preceding claim wherein the pH of the aqueous solution prior to oxidation is less than 2.0.

5. A process as claimed in claim 4 wherein the pH is 0.8

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to 1.5.

6. A process as claimed in any preceding claim wherein the oxidation stage is a one-step oxidation stage.

7. A process as claimed in any preceding claim wherein the oxidising agent comprises nitric acid and/or peroxide such as hydrogen peroxide.

8. A process as claimed in any preceding claim wherein the oxidation temperature is 110°C or lower, such as 90°C or lower, or 70°C or lower.

9. A process as claimed in any preceding claim wherein the oxidation step is effected at a temperature between 15°C to 50°C.

10. A process as claimed in any preceding claim wherein the oxidation time for the oxidation step is up to 3 hours, preferably up to 2 hours, more preferably up to 1.75 hrs, most preferably up to 1 hr.

11. A process as claimed in any preceding claim wherein after the oxidation step the concentration of ferrous ions in solution is less than 2.5% Fe^{2+}/Fe^{3+} ; preferably less than 1.25% Fe^{2+}/Fe^{3+} , more preferably less than 0.25% Fe^{2+}/Fe^{3+} .

12. A process as claimed in any preceding claim wherein the

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base comprises a hydroxide or bicarbonate of an alkali metal.

13. A process as claimed in any preceding claim wherein, during the hydrolysis step, iron (III) hydrolysis species $[\text{Fe}(\text{OH})_x]^{(3-x)+}$ and polynuclear complexes of iron (III) $[\text{Fe}_m(\text{OH})_n]^{(3m-x)n+}$ form as the polymeric form of ferric sulphate.

14. A process as claimed in any preceding claim wherein the hydrolysis stage is carried out immediately after the oxidation stage without removing or otherwise purifying the ferric sulphate formed after the oxidation stage.

15. A process as claimed in any preceding claim wherein in the finished product obtained by the process, the molar ratio of $[\text{OH}]^-$ to $[\text{Fe}^{3+}]$ is at least 0.1 : 1, preferably 0.2 : 1, more preferably 0.25 : 1, more preferably 0.1 - 0.45 : 1.

16. A process as claimed in any preceding claim wherein the hydrolysis stage is carried out at a temperature up to 50°C for a time up to 3 hours.

17. Use of polyferric sulphate (PFS) obtained by a process as claimed in any preceding claim as a coagulant or flocculant.

18. A method of treating water which comprises adding to the water a product obtained by a process as claimed in any

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one of claims 1 to 16.

19. A method as claimed in claim 18 which is a method of purifying and/or decolourising water.

20. A method as claimed in claim 18 which is a method of reducing pollutants in industrial and/or municipal wastewaters.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU,A,464 517 (NITTETSU MINING CO) 28 August 1975 see the whole document	1-3, 12, 17
A	FR,A,1 518 716 (SOC. DES ACCUMULATEURS FIXES ET DE TRACTION) 29 March 1958 see the whole document	1-3
A	US,A,2 905 533 (C.S. WEBB) 22 September 1959 see the whole document	1, 8

☐ Further documents are listed in the continuation of part C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" documents defining the general state of the art which is not considered to be of particular relevance

"B" earlier documents but published on or after the international filing date

"L" documents which may throw doubt on priority claim(s) or which is used to establish the publication date of another claim or other special reason (as specified)

"O" documents referring to an oral disclosure, use, exhibition or other means

"P" documents published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but used to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" documents consisting of the same patent family

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(54) **Method for preparing ferric polysulfate solutions**

(57) In order to prepare cheap ferric polysulfate sludge from scraps formed during cutting operations, dust originated from converters, blast furnace ash, neutralized sludge, and/or burned sludge thereof, which have never been reused, a method for preparing a ferric polysulfate solution is proposed, having a basically comprising a first step for dissolving dust originated from converters, blast furnace ash, scraps formed during cutting operation, neutralized sludge originated from waste water treatment or burned sludge thereof in a sulfuric acid solution containing trivalent iron in an amount ranging from 5 g/liter to 50 g/liter, at a temperature ranging from 60 to 95 °C, while controlling the molar ratio: SO_4/Fe in the resulting solution to a level of not less than 1.5 and not more than 1.75; and a second step for oxidizing the resulting solution.

EP 0 885 846 A1

Description

The present invention relates to a method for preparing a ferric polysulfate solution having a basicity starting from, for instance, scraps formed during cutting, dust originated from converters (converter dust), blast furnace ash, neutralized sludge originated from waste water treatment and/or burned sludge thereof, i.e., iron metal, ferrous hydroxide, iron oxides.

As methods for preparing ferric polysulfate, there have been proposed various methods such as a method previously proposed by the applicant of this invention (inventors: Yasuo Mitani and Gerd Hübner) and disclosed in Japanese Patent No. 842,085, in which ferrous sulfate is used and which comprises a step of oxidation while adjusting the molar ratio: SO_4/Fe in a ferrous sulfate solution to a level of not more than 1.5; a method disclosed in Japanese Patent Publication Hei-2-22012 (JP-B-22012), which comprises polymerizing sulfuric acid by adding H_2SO_4 to trivalent iron in an amount of not less than 3 moles and less than 4 moles per one mole of trivalent iron; and a method disclosed in Japanese Laid-open Hei-9-47205 (JP-A-947205) which comprises partially neutralizing ferric sulfate with dilute trivalent iron.

However, the method disclosed in Japanese Patent No. 842,085 suffers from such drawbacks that the resulting product has a high content of NO_3^- since the oxidation is carried out using oxygen in the presence of a nitrogen oxide as a catalyst and that this method requires a long time for the preparation of the desired product. Moreover, trivalent iron is used as a starting material in Japanese Patent Publication Hei-2-22012, but it has generally been known that trivalent iron is soluble in hydrochloric acid, but is hardly soluble in sulfuric acid. For this reason, this method suffers from such a problem that it is, in fact, difficult to ensure a sufficiently high level of a hydroxyl value while polymerizing sulfuric acid by the addition of sulfuric acid to trivalent iron in an amount of not less than 3 moles and less than 4 moles per mole of trivalent iron at such a high temperature on the order of about 90 °C. Furthermore, the method disclosed in Japanese Laid-open Hei-9-47205 suffers from a problem of low reproducibility in the quality of the resulting products and a problem of high cost of production thereof.

The inventors of this invention have conducted various studies, over a long period of time, to eliminate the foregoing problems associated with the conventional methods and as a result, have found out that:

(1) A ferric polysulfate solution having an Fe concentration ranging from 170 g/liter to 180 g/liter could be obtained when reacting a sulfuric acid solution containing trivalent iron with an iron-containing raw material such as converter dust, blast furnace ash, neutralized sludge, burned sludge thereof and/or scraps formed during cutting operations while controlling the molar ratio: SO_4/Fe to a level of not less than 1.50 and not more than 1.75, preferably not less than 1.60 and not more than 1.70;

(2) To prepare the foregoing solution, the reaction is carried out at a temperature of not less than 60 °C and not more than 95 °C, preferably not less than 65 °C and not more than 85 °C and particularly preferably not less than 70 °C and not more than 80 °C;

(3) The trivalent iron concentration of the basic sulfuric acid solution suitably ranges from 5 g/liter to 60 g/liter and this is because if the concentration is less than 5 g/liter, any desired effect cannot be achieved as will be seen from Fig. 1 which shows the relation between the trivalent iron concentration and the leaching out rate of Fe, while if it exceeds 50 g/liter, the content of trivalent iron may constitute 1/4 to 1/3 of the whole ferric polysulfate solution having an Fe content ranging from 170 g/liter to 180 g/liter and this may impair the economical merit of the foregoing method and the product cannot be commercialized without difficulty;

(4) A solution obtained through the foregoing reaction carried out under such a condition that the molar ratio: SO_4/Fe is controlled to a level of not less than 1.50 and not more than 1.75 comprises free acid, but the addition of a divalent iron component such as ferrous sulfate to the solution and the subsequent oxidation of the solution permit the control of the molar ratio: SO_4/Fe to a level of not more than 1.50 and it has been confirmed that the foregoing agent thus prepared would have the same effect achieved by the conventional ferric polysulfate products.

The present invention has been developed on the basis of the aforementioned findings and accordingly, the inventors of this invention have succeeded in putting the foregoing method into practical use by dissolving, as an iron-containing raw material, converter dust, blast furnace ash, ash (or burned sludge) obtained by burning sludge originated from waste water treatment, neutralized sludge obtained by neutralizing sludge originated from waste water treatment (neutralized sludge) and/or metallic iron such as scraps formed during cutting or metal-processing, which comprise trivalent iron components and are substituted for ferrous sulfate conventionally used, by means of a sulfuric acid solution containing trivalent iron in an amount ranging from 5 g/liter to 50 g/liter.

Specific examples, which were carried out using the iron-containing raw materials described above are listed in the following Table 1. For each raw material, a conventional product is prepared using a solution listed in the upper row in each column of Table 1 and whose trivalent iron content is 0 g/liter, while a product according to the present invention is prepared using a solution listed in the lower row and whose trivalent iron content is 5 g/liter. As will be seen from the

data listed in Table 1, the leaching out rate of Fe achieved when using the solution having a trivalent iron content of 8 g/liter is about 10% higher than that observed when the solution used is free of any trivalent iron.

Table 1

Raw Material	Comp. of Raw Material			Comp. of Solution			Rate of Leaching (%)	Leaching Temp. (°C)
	T-Fe (%)	Fe ²⁺ (%)	Fe ³⁺ (%)	SO ₄ /Fe ¹⁾	T-SO ₄ (g/liter)	Fe ³⁺ (g/liter)		
Converter Dust	57.1	21.8	35.3	1.60	501	0	85	80
	57.1	21.8	35.3	1.60	501	8	98	80
Blast Furnace Ash	24.5	10.1	14.4	1.60	501	0	89	80
	24.5	10.1	14.4	1.60	501	8	99	80
Burned Sludge ²⁾	50.4	7.3	43.1	1.60	501	0	75	80
	50.4	7.3	43.1	1.60	501	8	90	80
Scraps from Cutting	98.5	0.5	0.5	1.60	501	0	85	80
	98.5	0.5	0.5	1.60	501	8	85	80
Neutralized Sludge ³⁾	16.4	0.5	15.9	1.60	501	0	90	80
	16.4	0.5	15.9	1.60	501	8	98	80

1) Molar ratio: SO₄/Fe used during the reaction.

2) Product obtained by burning sludge originated from waste water treatment.

3) Product obtained by neutralizing sludge originated from waste water treatment.

Fig. 1 is a graph showing the relation between the trivalent iron concentration and the rate of iron leached out. Fig. 2 is a graph showing the effect of the trivalent iron concentration on the rate of iron-oxidation.

The details of the present invention will hereinafter be described on the basis of the following five specific Examples, but these Examples are given for simply illustrating the present invention and do not limit the technical scope of the present invention at all.

Example 1

Scraps (171 g) originated from cutting, as a raw material, whose overall iron content was 98.5% and comprising not more than 0.5% of divalent iron, not more than 0.5% of trivalent iron and the balance of metallic iron was dissolved in a sulfuric acid solution having a trivalent iron concentration of 8 g/liter (having an overall amount of SO₄ of 485.5 g, maintained at 60 °C) while adjusting the whole volume of the solution was equal to one liter. This resulted in the formation of a solution having an overall iron concentration of 178.4 g/liter and an overall SO₄ concentration of 485.5 g/liter.

To the resulting solution, there was added 263.0 g of ferrous sulfate (FeSO₄) followed by the oxidation thereof to thus give 1.3 liter of a ferric polysulfate solution having a basicity. The resulting solution was inspected for the storage stability and it was confirmed that the solution underwent any change even after it was stored over 6 months. Separately, the same procedures used above were repeated except for using a sulfuric acid solution substantially free of trivalent iron (the method according to Japanese Patent No. 842,085) to give a ferric polysulfate solution having an iron concentration of 160 g/liter. However, this latter method required a longer time for the oxidation as compared with the foregoing Example. The relation between the trivalent iron concentration and the rate of iron-oxidation was also examined. The results thus obtained are plotted on Fig. 2. The data plotted on Fig. 2 clearly indicate that the presence of trivalent iron in a concentration ranging from 5 g/liter to 50 g/liter permits the achievement of the same rate of oxidation within a time corresponding to about 0.5 to 0.8 times that required for the conventional method wherein the sulfuric acid solution is free of trivalent iron.

Table 2

	Composition		Specific Basicity Gravity	
	T-Fe (g/liter)	T-SO ₄ (g/liter)		
Conventional Product	160	380	1.45	0.22
Product of the Invention	176.4	485.5	1.52	0.29

The foregoing ferric polysulfate solutions prepared according to these methods were evaluated by a jar test carried out using waste water discharged from a papermaking and pulping factory (COD 104 ppm, SS 65 ppm, pH 7.18). The results thus obtained are summarized in the following Table 3.

Table 3

	Added Amount ppm	T-Fe ppm	pH	NaOH ppm	COD ppm	SS ppm
Conventional Solution	272	30	6.25	0	72	35
Solution of the Invention	453	50	5.31	16	43	<10
	240	30	6.20	0	64	28
	400	50	5.37	16	40	<10

Note: The final pH of the solution tested ranged from 6.2 to 6.6 and each supernatant collected after 10 minutes was used for the evaluation of each solution.

Example 2

Converter dust (377 g), as a raw material, whose overall iron content was 57.1% (having a divalent iron content of 21.8% and a trivalent iron content of 35.3%) was dissolved in a sulfuric acid solution having a trivalent iron concentration of 8 g/liter (having an overall amount of SO₄ of 583 g, maintained at 60 °C) and it was confirmed that 88% of iron was leached out. The resulting solution was found to have an overall iron concentration of 145.9 g/liter and an overall SO₄ concentration of 388.7 g/liter and the whole volume of the resulting solution was found to be 1.5 liter. To the resulting solution, there was added 189.8 g of ferrous sulfate followed by the oxidation thereof to thus give 1.6 liter of a ferric polysulfate having an overall iron concentration of 180.3 g/liter and an overall SO₄ concentration of 443.5 g/liter. The resulting solution was subjected to the same test carried out in Example 1 using the same waste water discharged from a paper-making and pulping factory and the same results were obtained.

Example 3

Blast furnace ash (902.5 g), as a raw material, whose overall iron content was 24.5% (having a divalent iron content of 10.1% and a trivalent iron content of 14.4%) was dissolved in a sulfuric acid solution having a trivalent iron concentration of 8 g/liter (having an overall amount of SO₄ of 583 g, maintained at 60 °C) and it was confirmed that 99% of iron was leached out. The resulting solution was found to have an overall iron concentration of 145.9 g/liter and an overall SO₄ concentration of 388.7 g/liter and the whole volume of the resulting solution was found to be 1.5 liter. To the resulting solution, there was added 189.8 g of ferrous sulfate followed by the oxidation thereof to thus give 1.6 liter of a ferric polysulfate having an overall iron concentration of 180.3 g/liter and an overall SO₄ concentration of 443.5 g/liter. The resulting solution was subjected to the same test carried out in Example 1 using the same waste water discharged from a paper-making and pulping factory and the same results were obtained.

Example 4

Neutralized sludge originated from waste water treatment (1361.7 g), as a raw material, whose overall iron content was 16.4% (having a divalent iron content of 0.5% and a trivalent iron content of 15.9%) was dissolved in a sulfuric acid solution having a trivalent iron concentration of 8 g/liter (having an overall amount of SO₄ of 583 g, maintained at 60 °C) and it was confirmed that 96% of iron was leached out. The resulting solution was found to have an overall iron concentration of 145.9 g/liter and an overall SO₄ concentration of 388.7 g/liter and the whole volume of the resulting solution

was found to be 1.8 liter. To the resulting solution, there was added 198.8 g of ferrous sulfate followed by the addition thereof and filtration through diatomaceous earth to thus give 1.4 liter of a ferric polysulfate having an overall iron concentration of 160.8 g/liter and an overall SO_4 concentration of 445.5 g/liter. The resulting solution was subjected to the same test carried out in Example 1 using the same waste water discharged from a paper-making and pulping factory and the same results were obtained.

Example 2

Slurried sludge originated from waste water treatment 2777 g, to a new material, whose overall iron content was 68.4% (having a diatomaceous earth content of 7.8% and a trivalent iron content of 48.1%) was dissolved in a sulfuric acid solution having a SO_4/Fe concentration of 10 g/liter (having an overall amount of SO_4 of 644.8 g, molar weight of 98.08) and 5 g/liter of trivalent iron was leached out. The resulting solution was found to have an overall iron concentration of 140.8 g/liter and an overall SO_4 concentration of 300.8 g/liter and the whole volume of the resulting solution was found to be 1.8 liter. To the resulting solution, there was added 198 g of ferrous sulfate followed by the addition thereof to thus give 1.8 liter of a ferric polysulfate having an overall iron concentration of 161.6 g/liter and an overall SO_4 concentration of 445.2 g/liter. The resulting solution was subjected to the same test carried out in Example 1 using the same waste water discharged from a paper-making and pulping factory and the same results were obtained.

Claims

1. A method for preparing a ferric polysulfate solution having a basically comprising a first step for dissolving dust originated from converters, blast furnace ash, neutralized sludge originated from waste water treatment, burned sludge thereof, or scraps formed during cutting operations in a sulfuric acid solution containing trivalent iron in an amount ranging from 5 g/liter to 80 g/liter, at a temperature ranging from 80 to 85 °C, while controlling the molar ratio: SO_4/Fe in the resulting solution to a level of not less than 1.5 and not more than 1.75; and a second step for oxidizing the resulting solution.
2. The method for preparing a ferric polysulfate solution according to claim 1 wherein trivalent iron or metallic iron is added to the solution prior to the initiation of the second step.

Fig. 1

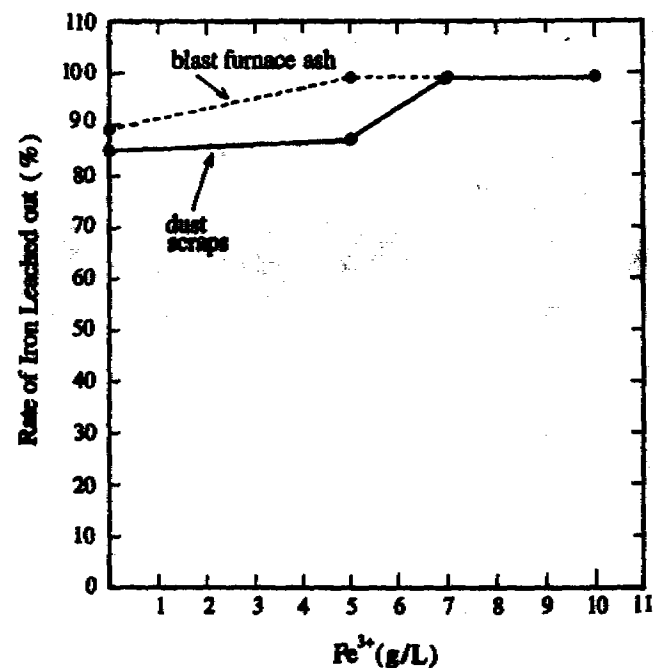
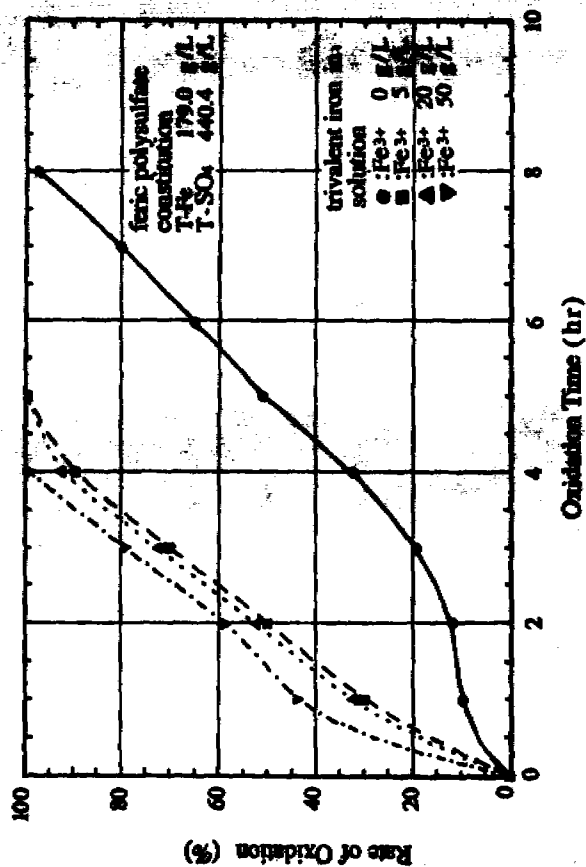


Fig. 2

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 88 10 7482

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to:	Relevant to the invention as claimed
A	US 4 707 349 A (NORSTEN NORSTEN G) 17 November 1987 • the whole document •	1	C01G49/14 C02F1/52
A	DATABASE MPI Section Ch, Week 9021 Derwent Publications Ltd., London, GB; Class E31, AN 90-162873 XP002077130 • SU 1 502 474 A (MINSEITOV S R) • 23 August 1989 • abstract •	1	
A	DATABASE MPI Section Ch, Week 8704 Derwent Publications Ltd., London, GB; Class D15, AN 87-027498 WP002077131 • JP 61 206228 A (NITTETSU MINING CO LTD) • 16 December 1986 • abstract •	1	
The present search report has been drawn up for all claims			INTERNATIONAL PUBLICATION NUMBER (PCT No.) C01G C02F
Place of search THE HAGUE		Date of completion of the search 10 September 1988	Searcher LJDBERECHT, E
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