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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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 Evento 001
 Actuación 430
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Patente de Invención ☒ Patente de Modelo de Utilidad ☐
Vía Nacional ☒
Vía PCT (fase nacional) ☐ Cap. I ☐ Cap. II ☐

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

- 1.1. Descripción: Folios: 6 tal como se radicó inicialmente
- 1.2. Reivindicaciones: Folios 7 tal como se radicó inicialmente
- 1.3. Dibujos: Folios 4 tal como se radicó inicialmente

2. Objeto de la invención

- Título de la solicitud (folio 1)
Procedimiento de obtención de un polímero natural para el tratamiento del agua
- Las reivindicaciones 1 a 5 de la solicitud en estudio se refieren a
- *El procedimiento de obtención está caracterizado por el uso de la materia prima Almidón dulce de yuca.*
- El anterior procedimiento (?) busca mejorar el tratamiento de agua
- La Clasificación Internacional de Patentes (IPC) para esta solicitud es C 02 F 1/00; C 08 L 3/00

3. De la solicitud de Patente

La solicitud se encuentra muy mal presentada y no sigue los requisitos exigidos por la ley, tal como se verá a continuación.

3.1. Descripción (Artículo 28 D. 486)

La descripción de la solicitud en estudio no viene como lo exige la legislación. El Artículo 28 de la Decisión 486 es claro en establecer que la descripción **deberá** divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla. La descripción de la invención **indicará** el nombre de la invención e **incluirá la siguiente información**:

- a) el sector tecnológico al que se refiere o al cual se aplica la invención;
- b) la tecnología anterior conocida por el solicitante que fuese útil para la comprensión y el examen de la invención, y las referencias a los documentos y publicaciones anteriores relativas a dicha tecnología;
- c) una descripción de la invención en términos que permitan la comprensión del problema técnico y de la solución aportada por la invención, exponiendo las diferencias y eventuales ventajas con respecto a la tecnología anterior;
- d) una reseña sobre los dibujos, cuando los hubiera;
- e) una descripción de la mejor manera conocida por el solicitante para ejecutar o llevar a la práctica la invención, utilizando ejemplos y referencias a los dibujos, de ser éstos pertinentes; y,
- f) una indicación de la manera en que la invención satisface la condición de ser susceptible de aplicación industrial, si ello no fuese evidente de la descripción o de la naturaleza de la invención.

Se evidencia que quien escribe la solicitud, desconoce sobre el tema de patentes. Ni la descripción ni los dibujos se encuentran bien presentados. Por consiguiente se sugieren los siguientes ítems tomados del Manual del Inventor.

La descripción de la invención cumple una función importante que es la de divulgar la invención, lo que significa que la invención debe estar descrita en una forma suficientemente clara y completa para que sea posible su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla. Estos dos requisitos se complementan ya que la comprensión de la invención es lo que la persona capacitada en la materia correspondiente puede entender acerca de la invención y llegar a evaluar el aporte que se hace a la tecnología, mientras que la ejecución comprende poder realizar paso a paso la invención.

Es responsabilidad del solicitante suministrar la información en la descripción de forma clara. La descripción debe estar escrita en el lenguaje común del campo técnico al cual pertenece la invención. Si un término tiene un significado distinto al que comúnmente se le da en el campo técnico, éste deberá indicarse, así como utilizar los signos y símbolos aceptados en el campo en cuestión para las fórmulas matemáticas y las fórmulas químicas. Las unidades de medida deben expresar su correspondencia en el Sistema Internacional de Unidades. No se acepta dentro de la descripción, el uso de nombres propios, genéricos, marcas o similares para

referirse a la materia objeto de la invención, a menos que estén definidos en la descripción. Si se incluyen dibujos, ellos deben estar al inicio descritos brevemente dentro de la descripción tal como: "Figura 1 muestra una vista lateral de la máquina empaquetadora; etc."

La descripción y los dibujos deben ser consistentes los unos con los otros al referirse a los signos, símbolos o números de referencia.

El propósito de la descripción es asegurar que por un lado, la solicitud contenga la suficiente información técnica para que una persona con conocimiento medio en el arte pueda poner en práctica la invención, y por el otro que esta divulgación sea suficiente para conocer el aporte que se está haciendo a la tecnología. Esto no se cumple en la presente solicitud.

Los dibujos, planos, figuras y representaciones gráficas tienen como finalidad contribuir a una mejor comprensión y divulgación de la invención, por lo tanto deberán tener ciertas características:

- deben tener una relación directa con la descripción;
- deben permitir visualizar las formas de ejecución descritas;
- la relación entre la descripción y los dibujos se debe hacer por medio de signos de referencia que se encuentran en ambos elementos y guarden una correspondencia;
- si dentro de la descripción han sido mencionadas algunas figuras, necesariamente deben estar incluidas;
- no deben considerarse figuras o dibujos que no hayan sido descritos;
- no deben considerarse símbolos o números que no hayan sido mencionados en la descripción;
- en lo posible, no deben incluirse textos o letreros;
- los diagramas esquemáticos y de flujo se consideran dibujos; y
- deben ser numerados individual y consecutivamente

Se le recomienda al solicitante que se asesore de una persona que conozca del arte de las patentes.

Por lo anterior, la descripción no cumple con el requisito de claridad y/o divulgación completa que permita su comprensión y ejecución de acuerdo al art. 28 de la Decisión 486 y/o art. 22 del Tratado PCT.

3.2. Reivindicaciones (Artículo 30 D. 486)

El capítulo reivindicatorio de la solicitud en estudio no viene como lo exige la legislación. El Artículo 30 de la Decisión 486 es claro en establecer 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 que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple."

Se evidencia que quien escribe la solicitud, desconoce sobre el tema de patentes. Las reivindicaciones se encuentran muy mal presentadas. Por consiguiente se sugieren los siguientes ítems tomados del Manual del Inventor.

Las reivindicaciones son la parte más importante de la solicitud, pues **definen la invención a proteger y delimitan el alcance de esa protección** (Art. 51). Es **fundamental que sean claras y concisas** (Art. 30), para que:

- se puedan comparar y diferenciar del estado de la técnica con el fin de verificar los requisitos de patentabilidad; y
- puedan determinar sin ambigüedad hasta dónde llegan los derechos del titular de la patente.

El requisito de claridad y concisión se aplica a cada reivindicación individualmente, así como al conjunto de todas.

Las reivindicaciones deben contener todas las características técnicas esenciales de la invención las cuales definen a la invención y la hacen o pudieran hacerla distintiva del estado de la técnica. Estas características esenciales definen la solución al problema técnico que intenta resolver la invención.

Para efectos del examen, no se toma en cuenta como característica técnica de la invención la inclusión de términos relativos a aspectos no técnicos, como por ejemplo las ventajas comerciales, dado que el resultado o fin alcanzado de la invención no es una característica esencial a estos efectos. Sin perjuicio de ello, la inclusión de elementos no técnicos pueden afectar la claridad de la reivindicación. Una reivindicación debe incluir no solamente una enumeración de elementos, sino también indicar su funcionamiento y la relación funcional entre los mismos cuando para la persona versada en la materia ello no se desprenda de forma obvia de la misma definición del elemento.

Por su estructura todas las reivindicaciones deben constar de dos partes. Una primera parte, el preámbulo, sirve para situar el objeto de la invención dentro de un contexto técnico, es lo que se conoce y sobre lo que no se reclama ningún privilegio. La segunda parte, o parte característica, define lo que se considera novedoso y se desea proteger. Estas dos partes están separadas por expresiones como 'caracterizado por' o similares.

El significado y alcance de las palabras de las reivindicaciones debe ser el que normalmente se les da en el área técnica de la solicitud, y tiene que ser claro para la persona versada en la materia con la sola lectura de las reivindicaciones. Si la palabra tiene un significado especial dado por una definición en la descripción, esta definición deberá incluirse en la reivindicación, siempre que esto sea factible.

Se deben evitar inconsistencias entre las reivindicaciones y la descripción inicialmente presentada puesto que la descripción debe servir para interpretar las reivindicaciones (Art. 51 D 486). Existen varios casos frecuentes de inconsistencia:

- inconsistencia verbal: la descripción dice que la invención está limitada por unas características y las reivindicaciones no están así limitadas.
- inconsistencia en cuanto a características esenciales: cuando de la descripción se desprende que una característica es esencial para la invención (forma parte de la solución al problema a resolver) y ésta no se encuentra en las reivindicaciones. En este caso se alega que las reivindicaciones no definen la materia que se desea proteger (Art. 30) y se pide la introducción de esas características esenciales en las reivindicaciones; y
- frases de carácter general que sugieren de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones o que se protege también un producto cuando las reivindicaciones son sólo de procedimiento.

No se puede admitir términos imprecisos del tipo "aproximadamente", "alrededor de" ya que en ese caso el alcance y ámbito de protección de la reivindicación deja

de ser precisa y por lo tanto clara y no permite una comparación con el estado de la técnica. Por las mismas razones no se admiten términos relativos del tipo "mayor", "delgado", "fuente" ya que no tienen un significado preciso. En ningún caso estos términos se pueden utilizar para distinguir la invención del estado de la técnica. En estos casos se deben sustituir estas expresiones por términos precisos o rangos concretos de valores. Las marcas registradas o nombres comerciales definen productos o proceso que pueden cambiar con el paso del tiempo aunque conserven el mismo nombre; por ello su uso en una reivindicación no está permitido ya que no permiten establecer el alcance de la reivindicación.

Como se menciona anteriormente, las reivindicaciones deben definir la invención por sus características esenciales, estructurales o funcionales. No se admite que la reivindicación defina la invención por el resultado a alcanzar (del tipo: "Aparato de destilación caracterizado porque tiene un rendimiento del 99%"), puesto que en realidad equivaldría a definir el problema técnico a resolver y el alcance de la reivindicación incluiría no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado.

El requisito de concisión del Art. 30 D 486 se aplica tanto a cada reivindicación individual como al conjunto de reivindicaciones. La finalidad de este requisito es evitar una excesiva complejidad para el examinador a la hora de analizar las reivindicaciones, y evitar que terceros no puedan ver claramente cuál es el alcance de las reivindicaciones por el excesivo número y complejidad de éstas.

El número de reivindicaciones necesarias se debe considerar teniendo en cuenta en cada caso la naturaleza de invención a proteger. Para efectos de claridad, las reivindicaciones se presentan numeradas de manera consecutiva.

Las reivindicaciones tienen que estar sustentadas en la descripción (Art. 30 D 486). Esto significa que el objeto de cada reivindicación tiene que tener su fundamento en la descripción y que su alcance no debe exceder más allá de lo justificado por el contenido de la descripción y los dibujos.

Se le recomienda al solicitante que se asesore de una persona que conozca del arte de las patentes, para la redacción de su solicitud.

Por lo anterior, el capítulo reivindicatorio no cumple con el requisito de definición, claridad, concisión o sustento por la descripción de acuerdo al art. 30 de la Decisión 486 y/o art. 22 Tratado PCT.

4. Determinación del Estado de la Técnica

De acuerdo a lo observado, **NO** es posible realizar una correcta **Determinación del Estado de la Técnica y Evaluación de los requisitos de patentabilidad**. Solo cuando se haya corregido adecuadamente la solicitud y se haya orientado de forma tal que sea claro lo que quiere ser protegido, sólo en ese momento esta oficina podrá elaborar una determinación correcta del estado de la técnica y una evaluación correcta de los requisitos de patentabilidad.

Sin embargo, se hará una primera aproximación al estudio de la solicitud

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 25 de mayo de 2007
- Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación
D1	US 4 502 961	Destabilization of sludge with hydrolyzed cassava starch flocculants	05.03.1985
D2	US 4 564 004	Hydrolyzed cassava starch flocculants	14.01.1986
D3	Varios documentos más		

5. Análisis de patentabilidad (Artículo 14 D. 486)

Teniendo en cuenta que esto es solo una aproximación al análisis de patentabilidad de la solicitud en estudio, dados los profundos problemas que adolece esta solicitud. **Se entiende** que el solicitante pretende protección sobre el uso de almidón de yuca en procesos de floculación.

En el presente caso el solicitante en realidad no ha definido proceso alguno sino simplemente un uso del almidón de yuca. En primer lugar, en Colombia los usos no se conceden. Se concede protección sobre productos o procedimientos donde los procedimientos son conjuntos de etapas que buscan un objetivo. En segundo lugar el uso de almidón de yuca como floculante es bien conocido en el arte. Dos documentos (D1 y D2), los cuales se anexan a este informe, revelan la utilización de almidón de yuca como floculante. Luego lo pretendido proteger por el solicitante ni es nuevo y se deriva directamente de la técnica conocida, por lo que la presente solicitud carecería de los requisitos de patentabilidad para que se le conceda el privilegio solicitado.

Si bien se han encontrado varios documentos más, estos dos son representativos del arte conocido por lo que no se hará alusión a otros escritos hasta tanto el solicitante no corrija su solicitud.

6. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

Nº	Documento Nº	Reivindicaciones afectadas	Requisito que afecta
D1	US 4 502 961	1 - 5	Novedad
			Nivel inventivo
D2	US 4 564 004	1 - 5	Novedad
			Nivel inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de SESENTA días contados a partir de la fecha de notificación de la presente comunicación. 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. El solicitante debe recordar que las puede pedir que se modifique la solicitud en cualquier momento del trámite, pero **la modificación no podrá implicar una ampliación de la protección que correspondería a la divulgación contenida en la solicitud inicial.**

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

Alix Carmenza Céspedes De Vergel
Directora de Nuevas Creaciones (C)

Concepto Técnico No. **3497**
Examinador Técnico **202003**

El anterior requerimiento fue notificado por fijación en lista, de fecha 24 NOV 2011

United States Patent [19]

Yong et al.

[11] Patent Number: 4,502,961

[45] Date of Patent: Mar. 5, 1985

[54] DESTABILIZATION OF SLUDGE WITH HYDROLYZED CASSAVA STARCH FLOCCULANTS

[75] Inventors: Raymond N. Yong, Beaconsfield; Amar J. Sethi, Baie D'Urfe, both of Canada

[73] Assignee: Suncor, Inc., Toronto, Canada

[21] Appl. No.: 562,355

[22] Filed: Dec. 16, 1983

[51] Int. Cl.³ C02F 1/54; C02F 11/14

[52] U.S. Cl. 210/728; 208/11 LE; 210/731; 210/907

[58] Field of Search 127/32, 33, 38, 70, 127/71; 208/11 LE; 210/609, 725, 727, 728, 731, 907; 536/102

[56] References Cited

U.S. PATENT DOCUMENTS

4,289,540 9/1981 Yong et al. 210/729
4,399,039 8/1983 Yong 210/728

4,414,117 11/1983 Yong et al. 210/727

FOREIGN PATENT DOCUMENTS

47-20601 6/1972 Japan 210/731
516294 12/1939 United Kingdom 127/33

OTHER PUBLICATIONS

Chemical Abstracts 85:126210s, 1976, Van Lonkhuyzen et al.

Primary Examiner—Peter Hruskoci
Attorney, Agent, or Firm—Paul Lipsitz

[57] ABSTRACT

Cassava starch hydrolyzed in the presence of insoluble metal salts formed in situ is a surprisingly effective flocculant for destabilizing dilute as well as thick sludge suspensions and is particularly effective when used in the treatment of bituminous tar sands tailings and in phosphate slimes.

5 Claims, No Drawings

DESTABILIZATION OF SLUDGE WITH HYDROLYZED CASSAVA STARCH FLOCCULANTS

BACKGROUND OF THE INVENTION

This invention relates to a novel hydrolyzed cassava starch composition and the process for making and using the same. More particularly, this invention relates to the discovery that cassava starch which is hydrolyzed in the presence of insoluble metal salts formed in situ is a very effective flocculant in destabilizing dilute as well as thick sludge suspensions.

In general, the suspensions destabilized by the starch composition of this invention are aqueous colloidal suspensions containing either clay minerals or metal oxides-hydroxides which are formed in large volume during mining operations in the recovery of such materials as coal, bitumen from tar sands, and metals and such suspensions are also formed in paper making operations. In the case of metal mining operations, suspensions known as slimes are formed, typically phosphate slimes or like materials produced in the mining of copper, nickel, and titanium. In coal and tar sands minings, for example, the mining effluent typically contains dilute or thick clay mineral suspensions. In paper making processes cellulosic fines, clays and other solids are present in the large volumes of liquids obtained.

In order to properly dispose of these voluminous mining discharges, regardless of their source, flocculants have conventionally been employed to destabilize these suspensions and thus permit the effective separation of water from solids. The use of wheat, corn and potato starch which has been hydrolyzed in the presence of metal salts formed in situ has been disclosed in U.S. Pat. No. 4,289,540 which issued on Sept. 15, 1981 and is hereby incorporated by reference. It has now been found that surprisingly superior flocculation is obtained if starch from the root of the cassava plant is used for preparing the hydrolyzed starch composition to give the starch flocculant.

OBJECTS OF THE INVENTION

It is, therefore, an object of this invention to provide an effective flocculant in destabilizing dilute as well as thick sludge suspensions, particularly colloidal suspensions obtained from mining operations.

It is a further object of our invention to provide an effective flocculating agent for treating tar sands tailing streams which carry suspended clay particles.

It is another object of our invention to provide such a flocculating agent which is economical to prepare and employ in the treatment of both tar sands tailing streams, and phosphate slimes obtained from phosphate mining operations.

In another aspect, it is yet another object of our invention to provide such a flocculant which is safe and easy to handle and which itself offers no ecologically undesirable side effects.

BRIEF SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that the foregoing and other objects may be achieved by employing a hydrolyzed cassava starch as a flocculant in destabilizing dilute as well as thick sludge suspensions. More particularly, it has been found that when these starches have been hydrolyzed in the presence of metal salts formed in situ there is formed a

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surprisingly effective composition for destabilizing such suspensions. Still more particularly, an especially effective flocculant composition may be prepared when calcium aluminophosphate cassava starch is used.

As aforesaid, the sludges being treated in accordance with this invention are aqueous colloidal suspensions containing either clay minerals or metal oxides-hydroxides which are formed during mining operations or other operations generating such suspensions. For sake of illustration, and simplicity only, the following description will be directed to a colloidal clay suspension obtained from bituminous tar sands mining. However, it will be understood that this invention is directed generally to the destabilization of all such suspensions.

PREPARATION OF THE HYDROLYZED STARCH

As aforementioned, the flocculant is prepared from a cassava starch which has been hydrolyzed in the presence of inorganic salts formed in situ.

The cassava starch itself is readily obtained from the cassava plant which is a tropical plant having swollen roots which store the starch. The cassava plant is also known as Manioc (Manihot utilisima), family Euphorbiaceae and in some areas is referred to as yucca ("Starch—Its Sources, Production and Uses", Charles A. Brantle, Reinhold Publishing Corp., 1953). Separation of the cassava starch from the root is well known in the art and need not be repeated in detail here. However, for the sake of completeness, the cassava starch used in the examples which follow was obtained in the following manner:

To 15 pounds of the peeled, diced cassava root 1.5 gallons of water was added to which 15 gms of potassium metabisulphite had also been added to prevent discoloration. The mixture was chopped with water in a blender at low speed just long enough to break up the cells (approximately 2 mins.). Then, the mass was filtered through a No. 60 mesh (250 micrometers) filter to remove the fibrous material from the starch suspension. The fibrous material was washed twice with fresh quantities of water and the starch suspensions combined and allowed to settle. Finally, the water was decanted and the starch was dried in an oven at 60° C. or sundried after which it was ready for use.

The hydrolysis of the cassava starch is achieved by simply heating the starch in the form of an aqueous suspension at about 85° to 95° C. and preferably at about 90° C. in the presence of soluble metal salts which will form an insoluble salt in situ. The starch should desirably be present in an amount of 1 gm to 10 gm per 100 ml of water, and preferably 2 to 6 gms per 100 mls of water.

Among the salts which may be employed during the hydrolysis are salts of metals such as sodium, potassium, ammonium, magnesium, calcium and aluminum. The respective anions may be sulfates, acetates, chlorides, nitrates, chlorates, bromides, iodides, thiocyanates, phosphates and the like. Particularly effective for purposes of this invention, as applied to tar sands tailing ponds, is calcium aluminophosphate cassava starch, although such other salts containing sodium, aluminum and phosphate ions and the like may also be used.

As indicated, the salts are added as soluble salts in order to form the insoluble salt in situ. Thus, for example, the preferred calcium aluminophosphate salt is advantageously formed in situ by the addition of speci-

fied amounts of calcium hydroxide, aluminum sulfate, and sodium phosphate to the aqueous cassava starch hydrolysis medium. In any event, the resulting salt should desirably be present in amounts of about 10 to 30 gms per 100 gms of starch, and preferably 15 to 20 gms per 100 gms of starch.

In the case of treatment of known phosphate slimes from phosphate mining operations with the flocculant of this invention, it will be understood that the presence or addition of a phosphate such as sodium phosphate, is not necessary and may be omitted from the salt preparation.

If desired, the cassava starch hydrolysate may be dried to remove water by freeze drying, air drying, spin drying or the like, to provide a solid powder composition which is convenient to handle, store and transport and which can readily be redispersed in water at the treatment site.

The following examples are provided for purposes of illustrating but not limiting the scope of this invention with respect to the preparation and use of the starch flocculants.

SYNTHESIS OF HYDROLYZED CASSAVA STARCH FLOCCULANT

Five grams of cassava starch is weighed into a flask fitted for refluxing. Two hundred milliliters of aqueous solution containing 0.617 gm of $Al_2(SO_4)_3 \cdot 18H_2O$, 0.704 gm $Na_3PO_4 \cdot 12H_2O$, and 0.463 gm $Ca(OH)_2$ is added to form calcium aluminophosphate in situ in the presence of the starch.

The suspension is refluxed at $90^\circ C \pm 5^\circ$ for two hours with simultaneous stirring. The hydrolysis is considered complete when the insoluble starch is converted into a colloidal solution. The volume is then made up to 250 ml with distilled water, thus giving a stock solution of 20,000 ppm of calcium aluminum phosphate cassava starch.

A preferred procedure for making the hydrolyzed cassava starch employs the method described in U.S. patent application Ser. No. 327,850, filed Dec. 7, 1981, which application is also incorporated herein by reference. In the preferred method, an aqueous suspension of the starch, alum and lime is heated until maximum viscosity of the suspension is obtained and immediately thereafter, the salt to be added (e.g. trisodium phosphate) is added to the mixture. The general procedure for such preferred method is as follows:

To 2.67 liters of tap water add 109.89 g cassava starch, 10.18 g lime and 6.78 alum and heat the mixture with stirring at a constant speed of 100 rpm at a rate of $0.5^\circ C$ per minute. Stirring is carried out with a Cole-Palmer Master Servodyne torque stirrer calibrated to give viscosity value. As heating and stirring are continued the viscosity is observed to rise significantly when a temperature of about $60^\circ C$ is reached and continues to rise until about $70^\circ C$ is reached, at which point it begins to fall and then 15.46 g of trisodium phosphate (Na_3PO_4) is immediately added. Heating and stirring at the same rate is continued until a temperature of 85° is reached, and then the heat is removed and the material is allowed to cool to room temperature. This hydrolyzed cassava starch suspension containing about 4% of the starch composition was used in the comparative tests which follow.

COMPARATIVE EXAMPLES

In order to compare and evaluate the efficiency of the cassava starch flocculants as settling aids, the test flocculants were used to treat tar sand tailings.

The tar sand tailings used contained 1.93% solids (w/w) which are largely silts and clays. The fines are quite dispersed and tend to remain in suspension for a long period of time.

Settling Tests of Tar Sand

Tailings Treated With Starch Flocculants

100 ml of the tar sand tailings was poured into a 100 ml cylinder and then 0.1 ml of alum (0.06 m-mole/l) was added to the tailings sample. The cylinder was inverted 5 times to mix the tailings with the alum. Then 0.25 ml of the 4% hydrolyzed cassava starch flocculant suspension was poured into the cylinder. The cylinder was again inverted five times. The dosage of treatment is approximately 100 PPM. The same procedure was used for a hydrolyzed wheat starch flocculant used for comparison. The treated samples were then allowed to settle in the cylinders without further disturbance. The sediment heights were recorded periodically until little change was observed.

4.3 Kynch Analysis of the Settling Tests

Results of the settling tests were evaluated in terms of Kynch analysis which gives a settling time called "ultimate time" (T_u). T_u is an indicator of the duration required for a sediment to reach close to the ultimate height and this parameter is used to evaluate the efficiency of settling aids in suspensions.

Another parameter for the expression of settling efficiency of sediments is called "Unit Area" which is defined as follows:

$$\text{Unit Area} = \frac{T_u}{C_o \times H_o}$$

where C_o = initial solids concentration (ton/cu. ft)

H_o = initial height (ft)

T_u = ultimate time (days)

Unit Area is expressed as sq. ft/ton/day. This is the area required to settle one ton of solids per day. Small Unit Area indicates efficient settling. The T_u and unit areas of the hydrolyzed cassava starch flocculant treated samples, a hydrolyzed wheat starch flocculant treated sample and an untreated sample are presented in Table I.

TABLE I

Tar Sand Tailings Treated With Flocculants

	T_u (Min)	Unit Area (sq. ft/ton/day)
Untreated	1440	284.63
Hydrolyzed Wheat Starch Flocculant*	98	191.73
Hydrolyzed cassava Starch Flocculant*	49	95.73

*Prepared by the preferred method of S.W. 327,850

As can be seen from the above table the hydrolyzed cassava starch flocculant of the invention is surprisingly superior to the hydrolyzed wheat starch flocculant.

The invention claimed is:

1. In the process for the destabilization of colloidal sludge suspensions containing clay minerals or metal

oxides-hydroxides, by treatment of said suspensions with an effective amount of a flocculating reagent to substantially separate water from suspended solids, the improvement wherein the flocculating reagent is a hydrolyzed cassava starch obtained by the aqueous hydrolysis of the starch in the presence of about 10 to 30 gms per 100 gms of starch of insoluble metal salts formed in situ and wherein the salts employed during the hydrolysis to form said insoluble salts are the soluble salts of metals selected from the group consisting of sodium, potassium, ammonium, magnesium, calcium and aluminum, and respective anions of said soluble salts are selected from the group consisting of sulfates, acetates,

chlorides, nitrates, chlorates, bromides, iodides, thiocyanates, and phosphates.

2. The process according to claim 1 wherein the sludge suspension is derived from bituminous tar sands mining operations.

3. The process according to claim 1 wherein the sludge suspension is a phosphate slime obtained from phosphate mining operations.

4. The process according to claim 1 wherein the hydrolyzed starch is calcium aluminophosphate cassava starch.

5. The process according to claim 1 wherein the concentration of flocculating reagent in the sludge suspension is controlled to provide at least 50 parts per million.

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United States Patent [19]

Yong et al.

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[45] Date of Patent: Jan. 14, 1986

[54] HYDROLYZED CASSAVA STARCH FLOCCULANTS

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[73] Assignee: Suncor, Inc., Toronto, Canada

[21] Appl. No.: 672,514

[22] Filed: Nov. 19, 1984

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[62] Division of Ser. No. 562,355, Dec. 16, 1983, Pat. No. 4,502,961.

[51] Int. Cl. C08B 30/12
[52] U.S. Cl. 127/33; 127/70
[58] Field of Search 127/32, 33, 38, 70, 127/71; 208/11 LE; 210/609, 725, 727, 728, 731, 907; 536/102; 106/130, 210

[56] References Cited

U.S. PATENT DOCUMENTS

4,289,540 9/1981 Yong et al. 210/729
4,399,039 8/1983 Yong 210/728
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47-20601 6/1972 Japan 210/731
516294 12/1939 United Kingdom 127/33

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[57] ABSTRACT

Cassava starch hydrolyzed in the presence of insoluble metal salts formed in situ is a surprisingly effective flocculant for destabilizing dilute as well as thick sludge suspensions and is particularly effective when used in the treatment of bituminous tar sands tailings and in phosphate slimes.

3 Claims, No Drawings

HYDROLYZED CASSAVA STARCH FLOCCULANTS

This application is a division of application Ser. No. 562,355 filed Dec. 16, 1983 now U.S. Pat. No. 4,502,961.

BACKGROUND OF THE INVENTION

This invention relates to a novel hydrolyzed cassava starch composition and the process for making and using the same. More particularly, this invention relates to the discovery that cassava starch which is hydrolyzed in the presence of insoluble metal salts formed in situ is a very effective flocculant in destabilizing dilute as well as thick sludge suspensions.

In general, the suspensions destabilized by the starch composition of this invention are aqueous colloidal suspensions containing either clay minerals or metal oxides/hydroxides which are formed in large volume during mining operations in the recovery of such materials as coal, bitumen from tar sands, and metals and such suspensions are also formed in paper making operations. In the case of metal mining operations, suspensions known as slimes are formed, typically phosphate slimes or like materials produced in the mining of copper, nickel, and titanium. In coal and tar sands mining, for example, the mining effluent typically contains dilute or thick clay mineral suspensions. In paper making processes ceebulosic fines, clays and other solids are present in the large volumes of liquids obtained.

In order to properly dispose of these voluminous mining discharges, regardless of their source, flocculants have conventionally been employed to destabilize these suspensions and thus permit the effective separation of water from solids. The use of wheat, corn and potato starch which has been hydrolyzed in the presence of metal salts formed in situ has been disclosed in U.S. Pat. No. 4,289,540 which issued on Sept. 15, 1981 and is hereby incorporated by reference. It has now been found that surprisingly superior flocculation is obtained if starch from the root of the cassava plant is used for preparing the hydrolyzed starch composition to give the starch flocculant.

OBJECTS OF THE INVENTION

It is, therefore, an object of this invention to provide an effective flocculant in destabilizing dilute as well as thick sludge suspensions, particularly colloidal suspensions obtained from mining operations.

It is a further object of our invention to provide an effective flocculating agent for treating tar sands tailing streams which carry suspended clay particles.

It is another object of our invention to provide such a flocculating agent which is economical to prepare and employ in the treatment of both tar sands tailing streams, and phosphate slimes obtained from phosphate mining operations.

In another aspect, it is yet another object of our invention to provide such a flocculant which is safe and easy to handle and which itself offers no ecologically undesirable side effects.

BRIEF SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that the foregoing and other objects may be achieved by employing a hydrolyzed cassava starch as a flocculant in destabilizing dilute as well as thick sludge suspensions. More particularly, it has been found

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that when these starches have been hydrolyzed in the presence of metal salts formed in situ there is formed a surprisingly effective composition for destabilizing such suspensions. Still more particularly, an especially effective flocculant composition may be prepared when calcium aluminophosphate cassava starch is used.

As aforesaid, the sludges being treated in accordance with this invention are aqueous colloidal suspensions containing either clay minerals or metal oxides/hydroxides which are formed during mining operations or other operations generating such suspensions. For sake of illustration, and simplicity only, the following description will be directed to a colloidal clay suspension obtained from bituminous tar sands mining. However, it will be understood that this invention is directed generally to the destabilization of all such suspensions.

PREPARATION OF THE HYDROLYZED STARCH

As aforesaid, the flocculant is prepared from a cassava starch which has been hydrolyzed in the presence of inorganic salts formed in situ.

The cassava starch itself is readily obtained from the cassava plant which is a tropical plant having swollen roots which store the starch. The cassava plant is also known as Manioc (Manihot utilisima), family Euphorbiaceae and in some areas is referred to as yucca ("Starch—Its Sources, Production and Uses", Charles A. Brantle, Reinhold Publishing Corp., 1953). Separation of the cassava starch from the root is well known in the art and need not be repeated in detail here. However, for the sake of completeness, the cassava starch used in the examples which follow was obtained in the following manner:

To 15 pounds of the peeled, diced cassava root 1.5 gallons of water was added to which 15 gms of potassium metabisulphite had also been added to prevent discoloration. The mixture was chopped with water in a blender at low speed just long enough to break up the cells (approximately 2 mins). Then, the mass was filtered through a No. 60 mesh (250 micrometers) filter to remove the fibrous material from the starch suspension. The fibrous material was washed twice with fresh quantities of water and the starch suspensions combined and allowed to settle. Finally, the water was decanted and the starch was dried in an oven at 60° C. or sundried after which time it was ready for use.

The hydrolysis of the cassava starch is achieved by simply heating the starch in the form of an aqueous suspension at about 85° to 95° C. and preferably at about 90° C. in the presence of soluble metal salts which will form an insoluble salt in situ. The starch should desirably be present in an amount of 1 gm to 10 gm per 100 ml of water, and preferably 2 to 6 gms per 100 mls of water.

Among the salts which may be employed during the hydrolysis are salts of metals such as sodium, potassium, ammonium, magnesium, calcium and aluminum. The respective anions may be sulfates, acetates, chlorides, nitrates, chlorates, bromides, iodides, thiocyanates, phosphates and the like. Particularly effective for purposes of this invention, as applied to tar sands tailing ponds, is calcium aluminophosphate cassava starch, although such other salts containing sodium, aluminum and phosphate ions and the like may also be used.

As indicated, the salts are added as soluble salts in order to form the insoluble salt in situ. Thus, for example, the preferred calcium aluminophosphate salt is

advantageously formed in situ by the addition of specified amounts of calcium hydroxide, aluminum sulfate, and sodium phosphate to the aqueous cassava starch hydrolysis medium. In any event, the resulting salt should desirably be present in amounts of about 10 to 30 gms per 100 gms of starch, and preferably 15 to 20 gms per 100 gms of starch.

In the case of treatment of known phosphate slimes from phosphate mining operations with the flocculant of this invention, it will be understood that the presence or addition of a phosphate such as sodium phosphate, is not necessary and may be omitted from the salt preparation.

If desired, the cassava starch hydrolysate may be dried to remove water by freeze drying, air drying, spin drying or the like, to provide a solid powder composition which is convenient to handle, store and transport and which can readily be redispersed in water at the treatment site.

The following examples are provided for purposes of illustrating but not limiting the scope of this invention with respect to the preparation and use of the starch flocculants.

SYNTHESIS OF HYDROLYZED CASSAVA STARCH FLOCCULANT

Five grams of cassava starch is weighed into a flask fitted for refluxing. Two hundred milliliters of aqueous solution containing 0.617 gm of $Al_2(SO_4)_3 \cdot 18H_2O$, 0.704 gm $Na_3PO_4 \cdot 12H_2O$, and 0.463 gm $Ca(OH)_2$ is added to form calcium aluminophosphate in situ in the presence of the starch.

The suspension is refluxed at $90^\circ C \pm 5^\circ$ for two hours with simultaneous stirring. The hydrolysis is considered complete when the insoluble starch is converted into a colloidal solution. The volume is then made up to 250 ml with distilled water, thus giving a stock solution of 20,000 ppm of calcium aluminum phosphate cassava starch.

A preferred procedure for making the hydrolyzed cassava starch employs the method described in U.S. patent application Ser. No. 327,850, filed Dec. 7, 1981, which application is also incorporated herein by reference. In the preferred method, an aqueous suspension of the starch, alum and lime is heated until maximum viscosity of the suspension is obtained and immediately thereafter, the salt to be added (e.g. trisodium phosphate) is added to the mixture. The general procedure for such preferred method is as follows:

To 2.67 liters of tap water add 109.89 g cassava starch, 10.18 g lime and 6.78 g alum and heat the mixture with stirring at a constant speed of 100 rpm at a rate of $0.5^\circ C$ per minute. Stirring is carried out with a Cole-Palmer Master Servodyne torque stirrer calibrated to give viscosity value. As heating and stirring are continued the viscosity is observed to rise significantly when a temperature of about $60^\circ C$ is reached and continues to rise until about $70^\circ C$ is reached, at which point it begins to fall and then 15.46 g of trisodium phosphate (Na_3PO_4) is immediately added. Heating and stirring at the same rate is continued until a temperature of 85° is reached, and then the heat is removed and the material is allowed to cool to room temperature. This hydrolyzed cassava starch suspension containing about 4% of the starch composition was used in the comparative tests which follow.

COMPARATIVE EXAMPLES

In order to compare and evaluate the efficiency of the cassava starch flocculants as settling aids, the test flocculants were used to treat tar sand tailings.

The tar sand tailings used contained 1.93% solids (w/w) which are largely silts and clays. The fines are quite dispersed and tend to remain in suspension for a long period of time.

Settling Tests of Tar Sand Tailings Treated With Starch Flocculants

100 ml of the tar sand tailings was poured into a 100 ml cylinder and then 0.1 ml of alum (0.06 m-mole/l) was added to the tailings sample. The cylinder was inverted 5 times to mix the tailings with the alum. Then 0.25 ml of the 4% hydrolyzed cassava starch flocculant suspension was poured into the cylinder. The cylinder was again inverted five times. The dosage treatment is approximately 100 PPM. The same procedure was used for a hydrolyzed wheat starch flocculant used for comparison. The treated samples were then allowed to settle in the cylinders without further disturbance. The sediment heights were recorded periodically until little change was observed.

4.3 Kynch Analysis of the Settling Tests

Results of the settling tests were evaluated in terms of Kynch analysis which gives a settling time called "ultimate time" (T_u). T_u is an indicator of the duration required for a sediment to reach close to the ultimate height and this parameter is used to evaluate the efficiency of settling aids in suspensions.

Another parameter for the expression of settling efficiency of sediments is called "Unit Area" which is defined as follows:

$$\text{Unit Area} = \frac{T_u}{C_0 \times H_0}$$

where

C_0 = initial solids concentration (ton/cu. ft)

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Unit Area is expressed as sq. ft/ton/day. This is the area required to settle one ton of solids per day. Small Unit Area indicates efficient settling. The T_u and unit areas of the hydrolyzed cassava starch flocculant treated samples, a hydrolyzed wheat starch flocculant treated sample and an untreated sample are presented in Table I.

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As can be seen from the above table the hydrolyzed cassava starch flocculant of the invention is surprisingly superior to the hydrolyzed wheat starch flocculant.

The invention claimed is:

1. A composition comprising a hydrolyzed cassava starch obtained by the aqueous hydrolysis of cassava starch in the presence of about 10 to about 30 gms per 100 gms of starch of insoluble metal salts formed in situ, and wherein the salts employed during the hydrolysis to form said insoluble salts are the soluble salts of metals selected from the group consisting of sodium, potassium, ammonium, magnesium, calcium, and aluminum, and the respective anions of said soluble salts are se-

lected from the group consisting of sulfates, acetates, chlorides, nitrates, chlorates, bromides, iodides, thiocyanates, and phosphates.

2. The composition according to claim 1 wherein the salt contains calcium, aluminum and phosphate ions.

3. The composition of claim 2 wherein the aqueous hydrolyzed starch is dried to form a solid composition.

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