10

Industria y Comercio

SUPERINTENDENCIA

Delegatura de propiedad Industrial

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PCT

SOLICITUD

PATENTE DE INVENCIÓN

21. **EXPEDIENTE No.** 08-83545

54. **TÍTULO** *CONCENTRACION DE SUSPENSIONES.*

51. **CLASIFICACIÓN INTERNACIONAL** *B01D 21/01*

71. **SOLICITANTE** *CIBA HODDING INC.*

DOMICILIO *BASILEA, SUIZA*

74. **APODERADO** *JIMENA ESCOBAR URIBE*

22. **BOGOTÁ, D. C.,**

(FORMA P-10)

Industria y Comercio
SUPERINTENDENCIA

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Act. 411 PRESENTACION Folios: 204

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
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1 SOLICITUD DE:

[X] Patente de Invención [ ] Patente de Modelo de Utilidad

[X] Capitulo I. [ ] Capítulo II

2 SOLICITANTE (71)	Nombre: **CIBA HOLDING INC.** Dirección: Klybeckstrasse 141, CH-4057 Basilea, Suiza. Nacionalidad o Domicilio: Basilea, Suiza Lugar de Constitución : Suiza Teléfono: Fax: E-mail	**IDENTIFICACIÓN** **C.C.** [ ] **NIT** [ ] **C.E.** [ ] **Otro** [ ] **Número**
3 REPRESENTANTE O APODERADO (74)	Nombre: JIMENA ESCOBAR URIBE Dirección: Carrera 11 No. 86-53, piso 6 Teléfono: 6 162051/61 Fax: 6 161889 E-mail: Jiescobar@clarkemodet.com.co	**IDENTIFICACIÓN** C.C. [X] NIT [ ] C.E. [ ] Otro [ ] Número 39.779.452**T.P** 68228
4 INVENTOR (ES) (72)	Nombre: **VER ANEXOS** Dirección: Nacionalidad o domicilio:	

5 PCT (86)

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6 TITULO (54) **CONCENTRACIÓN DE SUSPENSIONES.**

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	GRAN BRETAÑA	**18 de enero de 2006**	**0601000.3**

9 Comprobante de pago No. 08 - 59,035 **Fecha** 23 de julio de 2008

10 ANEXOS

- [x] Comprobante de pago de la tasa de presentación de la solicitud
- [ ] Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica
- [ ] Poderes si fuere el caso
- [x] Documento de cesión del inventor al solicitante o a su causante
- [ ] Declaraciones
- [x] Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- [x] Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- [ ] Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA).
- [ ] Traducción del examen preliminar internacional efectuado por la IPEA
- [ ] De ser el caso copia de contrato de acceso.
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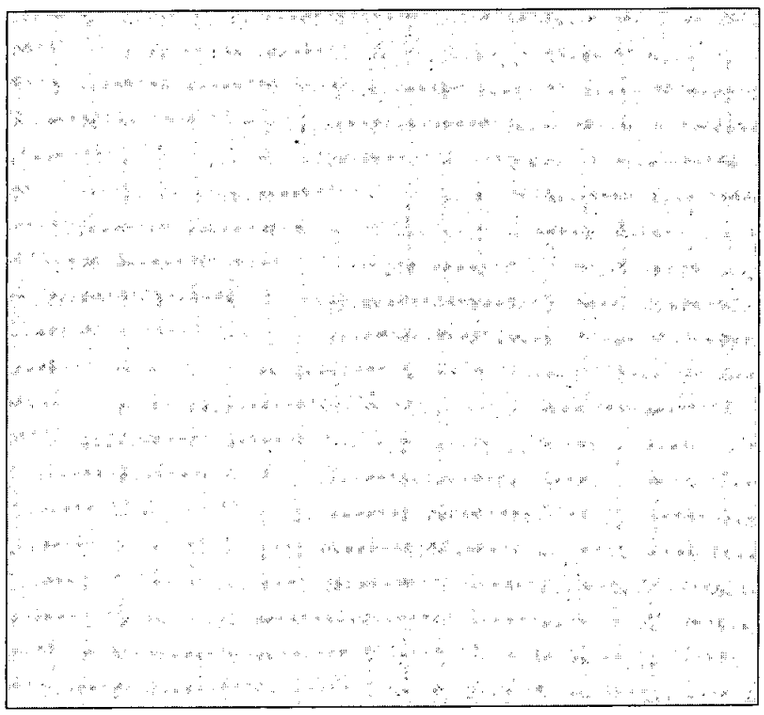
- [ ] De ser el caso, certificado de deposito del material biológico
- [ ] Arte final 12 X 12 .
- [ ] De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- [ ] De ser el caso, modificaciones efectuadas a la solicitud internacional
- [x] Otros *Opinión escrita. * Notificación de un cambio del titular,

11 FIGURA CARACTERÍSTICA



12 Solicito la concesión de la patente

NOMBRE: JIMENA ESCOBAR URIBE

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 08 - 59,035
FECHA : JULIO 23 DE 2008

***** C O N S I G N A C I O N *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	693136	23/07/2008	50,740,000.00

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

CANT.	RENTISTICO	CONCEPTO		TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN		501,000.00
		TOTAL :	$	501,000.00

SON: QUINIENTOS UN MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No._____

P-1315

ANEXOS

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P-1315

CO Case **MP/3-22379**

DOCUMENTO DE CESIÓN
ASSIGNMENT DOCUMENT

El (los) suscrito(s), en su calidad de inventor(es) de:
TRATAMIENTO DE SUSPENSIONES ACUOSAS
declara(n) que cede(n) y traspasa(n) todos los derechos que les correspondan en y sobre el invento atrás mencionado a
Ciba Holding Inc.
una compañia constituida y existente bajo las leyes de **Switzerland**, domicilada en **Klybeckstrasse 141, 4057 Basel, Switzerland.**
correspondiente al expediente No.
en cuanto se refiere a la República de Colombia.

The undersigned, as inventor(s) of:
CONCENTRATION OF SUSPENSIONS
hereby declare(s) that assign(s) all the rights in and to the aforementioned invention to
Ciba Holding Inc.
a company incorporated and existing in conformity with the laws of **Switzerland**, domiciled at **Klybeckstrasse 141, 4057 Basel, Switzerland.**
corresponding to file No.
as far as the Republic of Colombia is concerned.

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CO 12/01 (N&A)

APOSTILLE
(Hague Convention of 5 October 1961 / Convention de La Haye du 5 octobre 1961)

UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

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   Pays: Royaume-Uni de Grande-Bretagne et d'Irlande du Nord

   This public document / Le présent acte public

2. Has been signed by **C H P Atkinson**
   a été signé par

3. Acting in the capacity of **Notary Public**
   agissant en qualité de

4. Bears the seal/stamp of **The Said Notary Public**
   est revêtu du sceau/timbre de

Certified/Attesté

5. at London/à Londres

6. the/le **20 June 2008**

7. by Her Majesty's Principal Secretary of State for Foreign and Commonwealth Affairs /
   par le Secrétaire d'Etat Principal de Sa Majesté aux Affaires Etrangères et du Commonwealth.

8. Number/sous No **H820979**

9. Stamp:
   timbre:

10. Signature: **L Robinson**

FOREIGN AND COMMONWEALTH OFFICE LONDON

For the Secretary of State / Pour le Secrétaire d'Etat

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APOSTILLE

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7. Por:	Secretario de Estado Principal de su Majestad para las Relaciones Exteriores y la Commonwealth.
8. Bajo el No.	H820979
9. Sello / estampilla:	Oficina del Exterior y de la Commonwealth – Londres
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Documento No. 11-337

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11909

CUYA FIRMA APARECE EN EL
DOCUMENTO DESEMPEÑA
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2008 JUL -3 A 10:56

JEFE DE LEGALIZACIONES
BOGOTA D.C.

TRADUCCIÓN P-1315

Título: Concentración de suspensiones

Resumen: La presente invención se relaciona con un proceso para concentrar una suspensión acuosa de partículas sólidas que comprende los pasos de agregar al menos un floculante polimérico orgánico a la suspensión, formándose entonces sólidos floculados en donde se permite que los sólidos floculados formen una capa de sólidos formando así una suspensión más concentrada, dicho proceso comprende la adición de una cantidad efectiva de un agente que se selecciona de un grupo consistente en agentes radicales libres, agentes oxidantes, enzimas y radiación, en donde se aplica el agente a la suspensión antes o de manera sustancialmente simultánea a la adición del floculante polimérico orgánico y/o el floculante polimérico orgánico se agrega a la suspensión en un tanque y el agente es aplicado a la suspensión en el mismo tanque. El proceso es particularmente apropiado para la separación de sólidos y líquidos en donde se permite que los sólidos floculados se decanten por sedimentación en un tanque sedimentador por gravedad.

MP/3-22379/A 1

Concentración de suspensiones

La presente invención se relaciona con un proceso mejorado de floculación para la concentración de suspensiones. En particular, los sólidos floculados pueden sedimentarse para formar un lecho en el que pueden obtenerse más sólidos y/o un límite de fluencia reducido.

Es conocida la concentración de suspensiones de sólidos en líquidos acuosos usando floculantes, lo cual da como resultado la floculación de sólidos, lo cual facilita la separación de los sólidos del líquido. En muchos procesos los sólidos floculados se decantan para formar un lecho por sedimentación. En otros procesos la sedimentación puede facilitarse por desecación mecánica, por ejemplo en filtración por presión, centrifugación, por sedimentadores de correa y prensas de correa.

Los tipos de floculantes agregados a la suspensión frecuentemente dependerán del sustrato. Generalmente las suspensiones tienden a flocularse por polímeros de alto peso molecular. Ejemplos de esto se describen en WO-A-9314852 y US3975496 respecto a la floculación de suspensiones minerales tales como el barro rojo. Otras divulgaciones de floculantes poliméricos de alto peso molecular incluyen US 6447687, WO-A-0216495 y WO-A-02083258, que tratan sobre la floculación del fango de aguas residuales. Es sabido que a veces se agregan otros aditivos químicos para acondicionar la suspensión. Por ejemplo, las suspensiones pueden ser primero coaguladas por medio de un coagulante polimérico con una densidad de carga elevada tal como polyDADMAC o coagulantes inorgánicos incluyendo cloruro férrico.

Otros aditivos son usados también en el acondicionamiento de suspensiones. Por ejemplo a veces se agregan peróxidos a suspensiones tales como fangos de aguas residuales u otras suspensiones que contengan material orgánico para remover los agentes reductores con el fin de reducir olores, formación de gases o prevenir la putrefacción. En general tienden a agregarse peróxidos o agentes oxidantes para poder remover sustancias dañinas o indeseadas contenidas en la suspensión.

Generalmente la cantidad de peróxidos agregada es sólo suficiente para remover las sustancias y materiales indeseados, y generalmente los peróxidos u otros agentes oxidantes se incluyen en cantidades relativamente pequeñas.

Ejemplos de adición de peróxidos a fangos de aguas residuales se describen en JP56150481. Los peróxidos o los agentes oxidantes pueden también agregarse a otras suspensiones por razones similares, incluyendo el tratamiento de materiales dragados para remover contaminantes, tal como se describe en US 2003 121863 y JP 10109100. JP 11156397 describe un proceso de floculación de barro usando polímeros no iónicos y aniónicos, en donde el barro ha sido previamente tratado con un agente oxidante.

US 6733674 describe un método para desecar lodo agregándole una cantidad efectiva de una o más enzimas celulolíticas y uno o más oxidantes y uno o más floculantes para formar una mezcla en agua que es coagulada y floculada seguida luego de la separación de los sólidos del agua. Los ejemplos parecen indicar un paso de tiempo significativo entre la adición del oxidante y la floculación. Las enzimas al parecer estaban presentes a fin de degradar el material contenido en el lodo.

Las suspensiones son frecuentemente concentradas en un tanque de sedimentación por gravedad. Típicamente se alimenta un flujo continuo de suspensión en el tanque de sedimentación y

se trata con un floculante. Los sólidos floculados así formados se decantan para formar un lecho de subflujo sólido y el líquido acuoso sobrenadante fluye hacia arriba y es usualmente removido del tanque de sedimentación a través de un canal perimetral al nivel de la superficie del agua. Normalmente el tanque de sedimentación tiene una base cónica de manera que el subflujo pueda ser fácilmente removido del centro de la base. Adicionalmente un rastrillo rotativo ayuda en la remoción del subflujo de sólidos. Un proceso típico para concentrar suspensiones en un tanque de gravedad se describe en US4226714.

Pueden concentrarse varias suspensiones en tanques de sedimentación por gravedad, incluyendo suspensiones de sólidos orgánicos tales como aguas residuales y fangos de aguas residuales. También es común espesar o desecar suspensiones minerales usando tanques de sedimentación por gravedad.

En una operación típica de procesamiento de minerales, los sólidos de desecho son separados de los sólidos que contienen valores minerales en un proceso acuoso. La suspensión acuosa de sólidos de desecho frecuentemente contiene arcilla y otros minerales, a los que usualmente se denomina residuos. Estos sólidos a menudo son concentrados por un proceso de floculación en un tanque de sedimentación y se decantan para formar un lecho. En general es deseable remover la mayor cantidad de agua posible de los sólidos o lecho, para obtener un subflujo de mayor densidad y recolectar el máximo de agua del proceso. Es usual bombear el subflujo a un área de retención en la superficie, frecuentemente referida como foso o embalse de residuos, o alternativamente el subflujo puede ser desecado mecánicamente por medio de, por ejemplo, filtración al vacío, filtración por presión o centrifugación.

US 5685900 describe un proceso selectivo de floculación para beneficiar caolín de tamaño de partícula fino de bajo brillo con el fin de reducir una arcilla de caolín de alto brillo. El proceso incluye un paso de clasificación para recuperar la fracción de caolín en donde las partículas son al menos en un 90% en peso menores a 0.5µm. La fracción recuperada es sometida entonces a un paso de blanqueamiento para blanquear parcialmente los decolorantes orgánicos. La lechada obtenida es floculada selectivamente usando poliacrilamida aniónica de alto peso molecular o copolímero de acrilato y acrilamida. Este paso de floculación forma una fase sobrenadante que esta altamente concentrada con titanio contaminante, y una fase de arcilla floculada desprovista de titanio que contiene los decolorantes. Los flóculos son entonces tratados con ozono gaseoso con el fin de oxidar los remanentes orgánicos decolorantes y también para destruir el polímero floculante para restaurar el caolín a un estado disperso. Esto se logra pasando los sólidos floculados por un proceso de ozonización, usando preferiblemente una bomba de alto corte.

Divulgaciones similares se han hecho en WO 2004 071 989 y US 2006 0131243.

WO 2005 021129 divulga el control de la condición de una suspensión de partículas sólidas dentro de un líquido incluyendo aplicar uno o más estímulos a la suspensión. En esta divulgación el acondicionamiento es preferiblemente reversible e involucra floculación y/o coagulación en donde las fuerzas entre partículas pueden ser atractivas o repulsivas entre las partículas sólidas dentro del líquido. El estímulo puede ser uno o más aditivos químicos y puede por ejemplo ser un polielectrolito sensitivo al estímulo que puede ser absorbido en la superficie de partículas suspendidas en una cantidad suficiente para crear repulsión estérica o electrostática entre las partículas. En un caso un polielectrolito puede ser sustancialmente insoluble a valores

de pH en donde esta sustancialmente descargado logrando así la floculación de la suspensión.

También se describen polielectrolitos que responden a estímulos de temperatura. Así mismo se hace referencia a un método para controlar la consolidación de un lecho de partículas sólidas dentro de un líquido mediante la aplicación de uno o más estímulos al lecho. Cada uno de los estímulos efectúa un acondicionamiento operablemente reversible entre un estado inicial predominante antes de dicha aplicación de uno o más estímulos, y un estado acondicionante resultante de dichos uno o más estímulos. Los procesos descritos presentan mejoras en ciertas actividades de separación de sólidos y líquidos.

JP 11-46541 describe un polímero hidrofílico sensible a la temperatura agregado a una suspensión de partículas por debajo de una temperatura de transición con lo cual se forman flóculos por absorción y entrecruzamiento de partículas como un floculante convencional. La mezcla se calienta a una temperatura superior a la de transición y el polímero absorbido se torna hidrofóbico y las partículas suspendidas se vuelven hidrofóbicas y forman flóculos por interacción hidrofóbica. Se aplica presión externa apropiada en este momento y las partículas son fácilmente realineadas y se empieza a expeler agua de entre las partículas por la hidrofobicidad de éstas.

JP 2001 232104 describe un proceso similar a JP 11-46541 pero usando floculantes sensibles a la temperatura mejorados que son un polímero iónico sensible a temperatura por oposición a polímeros no iónicos que se absorben sobre partículas suspendidas y cuando el polímero se torna hidrofóbico a una temperatura como la del punto de transición hay fuertes capas de hidrato alrededor de los grupos iónicos, pero se impide la

adhesión de la capa hidratada entre los polímeros por interacción hidrofóbica.

Bertini, V. et al. Ciencia y Tecnología de las Partículas (1991), 9(3-4), 191-9 describe el uso de polímeros multifuncionales para la floculación con pH controlado de minerales de titanio. Los polímeros son copolímeros de radicales de vinilo que contienen funciones catechol y unidades de ácido acrílico. Los polímeros pueden cambiar su efecto de floculación a dispersión o inertes y viceversa, cambiando el pH.

Los floculantes sensibles al pH o a la temperatura proveen en principio control sobre el estado de floculación de una suspensión. Sin embargo, la escogencia del floculante tiene que ser apropiada para la suspensión en particular o lecho que vaya a ser floculado, y al mismo tiempo tiene que responder a un estímulo en particular para poder producir el acondicionamiento operablemente reversible. En algunos casos puede ser difícil hallar la elección correcta del floculante.

Frecuentemente quedará agua atrapada en los sólidos floculados, y esta agua es a menudo difícil de liberar, por lo cual se queda en el lecho. En tanto que los floculantes que responden al pH y a la temperatura pueden ser de ayuda en este problema, frecuentemente es difícil lograr una floculación satisfactoria a lo largo de un amplio rango de sustratos.

En procesos que involucran tanque de sedimentación por gravedad es deseable operar de forma en que el lecho tenga la mayor cantidad posible de sólidos que puedan ser removidos del tanque de sedimentación como subflujos. Normalmente el factor limitante es la capacidad del rastrillo en el tanque de sedimentación para mover los sólidos sedimentados, y sería por tanto deseable lograr un proceso que incremente la tasa

de separación de los sólidos de la suspensión y la remoción del subflujo.

De acuerdo con la presente invención nosotros proporcionamos un proceso de concentración de una suspensión acuosa de partículas sólidas que comprende los pasos de agregar al menos un floculante polimérico orgánico a la suspensión formando así sólidos floculados en donde se permite a los sólidos floculados formar un sustrato de sólidos, formando así una suspensión más concentrada en donde el proceso comprende la adición de una cantidad efectiva de un agente seleccionado de un grupo consistente de agentes radicales libres, agentes oxidantes, enzimas y radiación, donde el agente se aplica a la suspensión antes o de manera sustancialmente simultánea a la adición del floculante orgánico y/o el floculante polimérico orgánico se agrega a la suspensión en un recipiente y el agente se aplica a la suspensión en el mismo recipiente.

Hemos encontrado que la inclusión del agente mejora significativamente la eficiencia del proceso de concentración. Por concentración queremos significar que el contenido de sólidos de la suspensión es aumentado. Típicamente la concentración de una suspensión incluirá un proceso de desecación y un proceso de espesamiento, y similares.

Preferiblemente se permite a los sólidos floculados sedimentarse en un lecho de sólidos que también puede llamarse un sedimento. Más preferiblemente el proceso involucra la sedimentación en un tanque de sedimentación por gravedad y un sedimento o lecho es removido del tanque de sedimentación como un subflujo.

Sorprendentemente, el contactar el sustrato o lecho de sólidos con el agente permite un aumento significativo en la liberación de líquido acuoso.

Deseablemente el agente causa la fragmentación de la estructura floculada.

Preferiblemente, encontramos que la red floculada puede colapsar y a menudo ocupar un volumen menor que el que los sólidos sedimentados habrían ocupado con ausencia del agente.

En una forma el agente puede causar degradación del floculante polimérico orgánico. Se cree que la interacción química entre el floculante y los sólidos se altera de manera permanente como resultado de esta degradación de floculante polimérico. El polímero se puede degradar de tal forma que los sólidos tengan una red floculada reducida. En un aspecto la cadena de polímero puede descomponerse en cadenas más pequeñas lo cual induce un efecto dispersante sobre los sólidos. En algunos casos puede degradarse el polímero hasta el punto en que no tenga un efecto floculante sobre los sólidos. Se prefiere la degradación del floculante polimérico orgánico en conjunción con una degradación o reducción del tamaño de la estructura floculada. En una forma más preferida encontramos que la red floculada colapsa incrementando así el contenido de sólidos de un volumen dado.

En una forma preferida el agente causa una reducción en el límite de fluencia de un sustrato de sólidos formado por la acción del floculante orgánico. Más preferiblemente el sustrato de sólidos debe estar al menos un 30% por debajo del límite de fluencia de un sustrato de sólidos con un contenido equivalente de sólidos sin la adición del agente. Así el agente deseablemente causa una reducción en el límite de fluencia del sustrato o lecho de sólidos, y permite que se logren más sólidos y una remoción incrementada de subflujo.

Preferiblemente la reducción en el límite de fluencia será al menos un 50% inferior al límite de fluencia del sustrato de sólidos con un contenido equivalente de sólidos sin la adición del agente. Más preferiblemente la reducción del límite de fluencia será de al menos un 60 o 70% y a menudo al menos de 80 o 90%.

Inesperadamente también hemos encontrado que la fluencia puede reducirse por debajo del límite de fluencia de un sustrato de sólidos en un contenido equivalente de sólidos que no haya sido floculado y sin la adición del agente. Hasta ahora ha sido un concepto generalmente aceptado que la sedimentación de sólidos en la ausencia de floculación lograría un límite de fluencia inferior. Generalmente se creyó que un proceso que involucrara floculación siempre resultaría en un límite de fluencia más alto que en la ausencia de floculante porque el floculante tendería a retener los sólidos sedimentados en una estructura que tendería a incrementar el límite de fluencia. Consecuentemente, es particularmente sorprendente que un proceso que involucra el uso del floculante pueda resultar en un límite de fluencia inferior que el de una suspensión sedimentada sin el uso de floculante.

Preferiblemente las reducciones arriba mencionadas en el límite de fluencia se darán en combinación bien sea con una degradación o fragmentación de la estructura floculada y/o alternativamente en combinación con una degradación del floculante polimérico orgánico. Se prefiere especialmente que la degradación del floculante polimérico orgánico sea responsable de una degradación o reducción de tamaño de la estructura floculada lo cual a su vez causa una reducción del límite de fluencia del sustrato o lecho de sólidos.

En una forma preferida del proceso los sólidos floculados se decantan para formar un lecho y el agua se libera de la

suspensión, y hemos encontrado que la exposición de los sólidos floculados al agente causa un incremento en el agua extraída de la suspensión. Consecuentemente, encontramos que este aumento en el agua extraída también se acompaña de un incremento en los sólidos.

En un aspecto adicional, el agente puede ser un gas. Encontramos que la liberación de gas en un sustrato o lecho de sólidos puede aumentar la liberación de agua. En una forma preferida los sólidos floculados se decantan para formar un lecho y el agente está en contacto con los sólidos floculados o el lecho, y esto causa una liberación adicional de for y un incremento en los sólidos. Preferiblemente, el gas es liberado y forma burbujas de gas. Sin limitarse al campo teórico se cree que el gas puede por ejemplo causar la formación de canales o fisuras en el lecho de sólidos y facilitar la extracción del agua de la suspensión.

Los agentes que pueden desarrollar un gas incluyen los carbonatos, bicarbonatos y los peróxidos.

Se ha encontrado que el proceso de la presente invención aumenta la concentración de una suspensión, especialmente por sedimentación por gravedad. En este sentido la tasa de consolidación de los sólidos separados se incrementa. Adicionalmente, la movilidad de la fase concentrada, es decir, los sólidos decantados o sedimentados, puede mejorarse significativamente.

El agente puede ser uno o más compuestos químicos seleccionados de un grupo consistente en agentes radicales libres, agentes oxidantes y enzimas. Alternativamente o adicionalmente cuando el agente causa la degradación o fragmentación de la estructura floculada y/o la degradación del floculante polimérico orgánico y/o causa la reducción en el límite de fluencia del sustrato o lecho de sólidos, el

agente también puede incluir radiación. La radiación puede ser por ejemplo ultrasonido, radiación ionizante o radiación electromagnética. Cuando el agente libera gas puede alternativamente ser un aparato mecánico que libera burbujas de gas desde el interior de la capa de sólidos, especialmente cuando el sustrato es un sedimento o lecho.

El agente es preferiblemente seleccionado de un grupo consistente de agentes radicales libres, agentes oxidantes y enzimas.

Se ha encontrado que la incorporación de un agente de radicales libres o un agente oxidante en el proceso de floculación resulta en una fase de compactación más rápida, y/o en una viscosidad reducida del sustrato o lecho de sólidos, por ejemplo, sedimentos con un contenido correspondiente de sólidos, de tal forma que pueda lograrse un contenido más alto de sólidos sin exceder la máxima viscosidad que pueda tolerar el equipo encargado de realizar el proceso de remoción. En una modalidad adicional se ha encontrado que las enzimas producen un efecto similar. Este es el caso particular cuando el polímero es un polímero natural o semi-natural, por ejemplo un polisacárido que pueda haber sido modificado, y la enzima seleccionada sea conocida por degradar el polímero natural o semi-natural.

Agentes radicales libres apropiados incluyen compuestos químicos seleccionados del grupo consistente en sulfato ferroso de amonio, nitrato de amonio de cerio, etc.

También puede ser deseable utilizar activadores conjuntamente con agentes de radicales libres, los cuales en ciertos casos pueden acelerar la generación de radicales. Típicamente, tales activadores incluyen amino carboxilatos y diaminas, EDTA cúprico (ácido tetra acético de etilene diamina) y azúcares reductores como fructosa y lactosa.

Cualquier agente oxidante convencional puede ser usado. Los agentes oxidantes pueden ser sustancias químicas seleccionadas del grupo consistente de cloro, metales de transición u otros compuestos de metal en alto estado de oxidación, tales como compuestos de cromo, manganeso, hierro y cobre, cada uno de los cuales incluye sustancias que son poderosos agentes oxidantes, tBHP (hidro butil peróxido terciario), sulfito de sodio, compuestos de bisulfito, persulfato de amonio, perborato de sodio, hipoclorito de sodio y ozono.

Se ha encontrado que el uso de ozono, peracéticos, perboratos, percarbonatos y persulfatos es particularmente efectivo para propósitos oxidantes.

Puede usarse cualquier enzima adecuada capaz de actuar sobre el floculante polimérico orgánico, particularmente como un polímero natural. Típicamente, tales enzimas incluyen hidrolasas. Las encimas adecuadas incluyen proteasas, las cuales descomponen proteínas; glicolasas, que descomponen azúcares; pectinasas que descomponen pectinas; amilasas que degradan almidón; estearasas que degradan enlaces de ésteres; celulasas que descomponen celulosa y compuestos de celulosa; glucosidasas y galactosidasas o azúcares degradantes. Otras hidrolasas pueden modificar la superficie de otros floculantes poliméricos, incluyendo por ejemplo poliamidas y poliésteres. Otras enzimas incluyen depolimerasas que descompondrán polímeros, particularmente polimeros microbiológicamente generados tales como poliésteres. Las enzimas preferidas incluyen amilasas, celulasas, galactomanasas. En general, éstas son apropiadas para ser usadas con polímeros naturales o semi-naturales como por ejemplo almidón, CMC (carboxi metil celulosa), guar, alginatos, pectinatos y carragenatos de goma sulfatada. Otras

enzimas específicas son conocidas porque actúan sobre el chitosan.

Los agentes preferidos para ser usados en la presente invención son los peróxidos. Un peróxido particularmente preferido es el peróxido de hidrógeno.

En el proceso el agente y el floculante polimérico orgánico pueden agregarse a la suspensión secuencial o simultáneamente. Algunas operaciones pueden funcionar mejor si el agente se agrega en forma subsiguiente al floculante polimérico. Esto puede ser así especialmente si el agente actúa relativamente rápido, ya que debe permitirse el tiempo suficiente para sustancialmente formar primero la estructura floculada antes de que tengan lugar los efectos sustanciales del agente. No obstante, con éste orden de adición el floculante polimérico orgánico debe agregarse a la suspensión en un tanque y el agente se aplica a la suspensión en el mismo tanque. En este caso se prefiere que el agente se agregue al sustrato o lecho de sólidos. Típicamente este tanque puede ser un tanque de sedimentación, como por ejemplo un tanque de sedimentación por gravedad usado para la sedimentación de sólidos suspendidos.

Sin embargo, en muchas situaciones se prefiere que el agente se aplique a la suspensión antes de o en forma sustancialmente simultánea a la adición del floculante polimérico orgánico. Sin limitarse a la teoría se piensa que agregar el agente antes de cualquier formación sustancial de la estructura floculante asegurará que el agente se distribuya hacia todos los sólidos floculados. La adición del agente y el floculante simultáneamente puede también tener la ventaja de un único punto de adición, especialmente si el agente y el floculante están premezclados. Sin embargo, con mezclas de agentes y floculantes puede ser necesario

asegurarse que la mezcla se aplique a la suspensión antes de cualquier efecto destructivo del agente sobre el floculante.

El agente debe aplicarse en una cantidad efectiva. Preferiblemente, debe agregarse una cantidad suficiente que asegure que causará al menos uno de:
(i) fragmentación de la estructura floculada; y/o
(ii) degradación del floculante polimérico orgánico ; y/o
(iii) causar una reducción del límite de fluencia del sustrato de sólidos por debajo del límite de fluencia del sustrato de sólidos con un contenido equivalente de sólidos que no haya sido floculado y sin la adición del agente; y/o
(iv) permitir un incremento del contenido de sólidos de al menos el 5% en peso del sustrato con un límite de fluencia dado comparado con un sustrato que tenga el mismo límite de fluencia de un proceso equivalente pero con la ausencia del agente.

La cantidad de agente variará de acuerdo con las condiciones específicas del proceso, el tipo de sustrato y el floculante. Preferiblemente el agente debe estar presente en una cantidad de al menos 1 ppm basado en el peso del agente sobre el volumen de la suspensión. El agente puede ser efectivo en niveles bajos, por ejemplo entre 1 y 10 ppm. Generalmente el agente se agregará en una cantidad de al menos 100 ppm y en algunos casos puede ser de al menos 1000 ppm basado en el peso de los sólidos en la suspensión. En algunos casos puede ser deseable agregar niveles del agente significativamente más altos, por ejemplo tanto como 40.000 o 50.000 ppm o más. Las dosificaciones efectivas usualmente estarán en el rango entre 150 y 20.000 ppm, y especialmente entre 1.000 y 15.000.

Más preferiblemente el incremento del agua extraída del sustrato o lecho y el incremento de sólidos del sustrato o lecho se acompaña de una disminución en el límite de fluencia. Preferiblemente encontramos que el límite de

fluencia del sustrato o lecho es menor que un sustrato o lecho con contenido equivalente de sólidos en el que los sólidos floculados no sean expuestos al agente.

Se sabe que en general los sólidos en las suspensiones a menudo se decantan sin la adición de floculantes. El floculante ocasiona floculación cruzada de los sólidos e incrementa la tasa a la que los sólidos se decantan para formar un lecho. Por tanto en situaciones de sedimentación convencional por gravedad se logra una tasa mejorada de sedimentación libre y la compactación inicial por el uso de floculantes poliméricos, y opcionalmente coagulantes. En tal proceso las partículas sólidas individuales tienden a juntarse para formar agregados que tienen una densidad más favorable en proporción al área superficial. Estos agregados pueden sedimentarse para formar un lecho compacto del cual el agua puede luego removerse por percolación hacia arriba. De esta forma el lecho progresivamente incrementa su contenido de sólidos sobre un período extenso de tiempo hasta que se alcance la concentración de sólidos deseada en el lecho y el material del lecho pueda ser removido.

Desafortunadamente, en general la viscosidad o límite de fluencia de los sólidos sedimentados floculados en procesos convencionales tiende a ser significativamente más alta que los sólidos sedimentados con ausencia del floculante. Esto tiende a hacer el proceso de remoción por barrido y bombeo progresivamente más difícil. De otro lado, no sería práctico concentrar una suspensión en ausencia de floculante, ya que esto tomaría un tiempo extremadamente largo, especialmente en un tanque de sedimentación gravimétrico que se apoye en la sedimentación libre.

En el proceso de acuerdo con esta invención hemos encontrado que puede lograrse una fase más rápida de compactación. Adicionalmente se ha encontrado que el presente proceso

tiende a resultar en una viscosidad o límite de fluencia significativamente reducidos del sustrato de sólidos o lecho como resultado del tratamiento con el agente. En particular encontramos que el límite de fluencia es no sólo menor que en el proceso equivalente en ausencia del agente, sino que el límite de fluencia puede ser tan bajo o más bajo que los sólidos sedimentados en ausencia del floculante. En algunos casos encontramos que el proceso resulta en un sustrato o lecho de sólidos con un límite de fluencia significativamente por debajo del de los sólidos sedimentados en ausencia del floculante. Esta propiedad inesperada de los sólidos sedimentados facilita la remoción de un subflujo de sólidos mientras que al mismo tiempo asegura la rápida sedimentación de los sólidos. Más aún, se prefiere que el proceso se opere permitiendo que el contenido de sólidos del lecho consolidado se incremente significativamente por encima del que puede ser tolerado por el equipo en ausencia del agente. En este sentido el lecho consolidado puede aún ser operado al máximo límite de fluencia del equipo pero allí el contenido de sólidos es significativamente mayor que el del lecho en un proceso sin el agente.

El límite de fluencia del sustrato de sólidos incluyendo el lecho sedimentado variará de acuerdo con el sustrato. Típicamente el máximo límite de fluencia de un lecho sedimentado que puede tolerar un equipo convencional es usualmente no mayor a 250 Pa. Dentro de las capacidades del equipo existente no podría ser posible incrementar los sólidos usando el proceso convencional por cuanto el límite de fluencia sería demasiado alto. Se ha encontrado que el proceso de la invención usando el agente reduce el límite de fluencia en al menos un 10% y usualmente al menos en un 50%, y en algunos casos tanto como un 80 o 90% o más. De otro lado, puede permitirse el incremento en el contenido de sólidos del sustrato o lecho producido de acuerdo con la invención en un 5% y algunas veces más del 10% sin exceder el

máximo límite de fluencia que puede tolerar el equipo. En algunos casos puede ser posible incrementar los sólidos hasta en un 15 o 20% más en comparación con un sustrato o lecho que tenga el mismo límite de fluencia obtenido por el proceso equivalente pero sin el agente.

El porcentaje ne peso real del subflujo de sólidos que puede lograrse con un límite de fluencia aceptable varía considerablemente dependiendo del constituyente y el tamaño de las partículas de los sólidos suspendidos, y también de la edad y sofisticación del equipo de sedimentación. Puede ser tan bajo como 12% (típicamente fosfato de cieno de Florida) pero usualmente entre alrededor del 20% y el 50%.

El límite de fluencia se mide con un reómetro Brookfield R/S SST a temperatura ambiente de laboratorio de 25°C usando el programa de software RHEO V2.7 en un modo de Tasa de Corte Controlado. La rotación de una Veleta spindal (veleta 50_25 a un tamaño de tanque de 3 a 1) en pasos de 120 incrementos iguales de 0.025 rpm generan una aplicación progresiva de Tasa de Corte incrementada.

El límite de fluencia se define como el máximo esfuerzo cortante antes del comienzo del corte. El límite de fluencia se calcula por regresión linear de los 4 puntos de medida con Tasa de Corte > 0.1 1/s y cálculo subsiguiente de la interceptación del eje de Tau (Pa) para Tasa de Corte = 0.

La invención es aplicable a cualquier actividad de separación de sólidos y líquidos en la que los sólidos sean separados de una suspensión. Esto puede incluir por ejemplo procesos que involucren sedimentación, centrifugación, filtración por presión, prensado por banda o sedimentación por banda. La invención es particularmente benéfica en los procesos de sedimentación. Los procesos particularmente preferidos involucran someter la suspensión a floculación en un tanque

de sedimentación gravimétrico. En tales procesos los sólidos forman un sustrato compacto de sólidos concentrados, que en general será significativamente más alto que aquel en ausencia del agente.

Los sólidos floculados resultantes del proceso pueden formar un subflujo que puede ser removido de la zona de floculación y sedimentación. En muchas instancias los sólidos floculados forman un subflujo que es entonces transferido al área de eliminación.

Como se indicó anteriormente, la invención es generalmente aplicable a los procesos de separación de sólidos y líquidos. Por tanto la suspensión puede comprender material orgánico incluyendo por ejemplo fango de aguas residuales o material celular de procesos de fermentación. La suspensión puede también ser una suspensión de material celulósico, como por ejemplo sedimentos de procesos de fabricación de papel. Preferiblemente la suspensión es una suspensión acuosa que contiene partículas de minerales.

En una modalidad más preferida de la invención el proceso involucra el tratamiento de suspensiones acuosas resultantes del procesamiento de minerales de minería y otros desechos de minería, como por ejemplo industrias del carbón tales como arenas de hulla y alquitrán que comprenden suspensiones de partículas de minerales, especialmente arcillas. Por tanto, en este aspecto preferido del proceso la suspensión acuosa se deriva de operaciones de procesamiento de minerales o energía y/o capas de residuos. Por procesamiento de energía queremos decir preferiblemente procesos en los que el sustrato involucra la separación de materiales útiles como combustibles.

Un aspecto particularmente preferido del proceso involucra suspensiones seleccionadas de operaciones de minería y

refinación del grupo consistentes de bauxita, metales básicos, metales preciosos, hierro, níquel, carbón, arenas minerales, arenas de alquitrán, caolín, diamantes y uranio.

Preferiblemente los sólidos suspendidos en la suspensión deben ser al menos 90% en peso superiores a 0.5 micrones. Frecuentemente las partículas en la suspensión serán al menos 90% en peso de al menos 0.75 micrones y preferiblemente al menos 90% en peso de al menos uno o dos micrones. Típicamente las partículas suspendidas pueden tener un tamaño de al menos 90% en peso hasta de 2mm y usualmente al menos 90% en peso dentro del rango superior a 0.5 micrones a 2mm. Preferiblemente las partículas suspendidas serán al menos 90% en peso hasta 70 micrones, especialmente al menos 90% en peso dentro del rango de entre uno o dos micrones y uno o dos milímetros.

Las suspensiones con frecuencia contendrán al menos 5% de partículas de sólidos suspendidos en peso y podrán contener tanto como 30% o más. Preferiblemente las suspensiones contendrán al menos 0.25% y más preferiblemente al menos 0.5%. Usualmente las suspensiones contendrán entre 1% y 20% de sólidos suspendidos en peso.

Las dosis apropiadas de floculante polimérico orgánico fluctúan de 5 gramos a 10.000 gramos por tonelada de materiales sólidos. Generalmente la dosificación apropiada puede variar de acuerdo con el material específico y el contenido de sólidos materiales. Las dosificaciones preferidas se encuentran en un rango de 10 a 3.000 gramos por tonelada, especialmente entre 10 y 1.000 gramos por tonelada, en tanto que dosificaciones más preferidas fluctúan entre 60 a 200 o 400 gramos por tonelada.

La solución polimérica acuosa puede ser agregada en cualquier concentración adecuada. Puede ser deseable emplear una

solución relativamente concentrada, como por ejemplo de hasta 10% o más en base al peso de polímero. Usualmente sin embargo puede ser deseable agregar la solución polimérica a una concentración más baja para minimizar los problemas resultantes de la viscosidad de la solución polimérica y para facilitar la distribución del polímero en toda la suspensión. La solución polimérica puede agregarse en una concentración relativamente diluida, como por ejemplo tan baja como 0.01% en peso del polímero. Típicamente la solución polimérica se usará normalmente en una concentración entre 0.05 y 5% en peso del polímero. Preferiblemente la concentración de polímero estará en un rango entre 0.1% a 2 o 3%. Más preferiblemente la concentración fluctuará de 0.25% a más o menos 1% o 1.5%. Alternativamente el floculante polimérico orgánico puede ser agregado a la suspensión en la forma de partículas secas, o al contrario, como una fase inversa de emulsión o dispersión. Las partículas secas del polímero se disolverán en la suspensión acuosa y la fase inversa de emulsión o dispersión se reversará directamente en la suspensión acuosa en la cual entonces el polímero se disolverá.

El proceso de acuerdo con la invención presenta tasas de sedimentación mejoradas. Se ha encontrado que puede llegarse a una tasa de sedimentación entre 2 y 30 m/hora. Adicionalmente, encontramos que el proceso permite una remoción mayor al 99% en peso de los sólidos suspendidos dentro de la suspensión. Además el proceso permite un incremento en la concentración de sedimentos sólidos mayor al 10% en peso en comparación con los procesos convencionales en los que se opera sin el agente. Más preferiblemente se obtiene límite de fluencia de sedimentos reducido, en comparación con los mejores procesos convencionales.

El floculante polimérico orgánico puede incluir polímeros de alto peso molecular que sean catiónicos, no-iónicos,

aniónicos o anfotéricos. Típicamente si el polímero es sintético debe exhibir una viscosidad intrínseca de al menos 4 dl/g. No obstante, preferiblemente el polímero tendrá una viscosidad intrínseca significativamente más alta. Por ejemplo, la viscosidad intrínseca puede ser tan alta como de 25 o 30 dl/g o superior. Típicamente la viscosidad intrínseca puede ser al menos 7 y usualmente al menos 10 o 12 dl/g y puede ser tan alta como 18 o 20 dl/g.

La viscosidad intrínseca de los polímeros puede determinarse preparando una solución acuosa del polímero (0.5-1% p/p) basada en el contenido activo del polímero. 2 g de esta solución polimérica al 0,5-1,0% se diluye a 100 ml en un frasco volumétrico con 50 ml de solución de cloruro de sodio 2M que se regula a pH 7.0 (usando 1.56 g de fosfato de dihidrógeno de sodio y 32.26 g de fosfato de hidrógeno de disodio por litro de agua deionizada y todo se diluye a la marca de 100 ml con agua deionizada. La viscosidad intrínseca de los polímeros se mide usando un viscómetro Número 1 de nivel suspendido a 25°C en 1 M de solución salina amortiguada.

Alternativamente, el floculante polimérico orgánico puede ser un polímero natural o semi-natural. Los polímeros naturales o semi-naturales típicos incluyen los polisacáridos. Esto incluye el almidón catiónico, el almidón iónico, el almidón anfotérico y el chitosan.

Una clase preferida de polímeros incluye por ejemplo los polisacáridos como el almidón, la goma guar o dextrán, o un polímero semi-natural como carboximetil celulosa o hidroxietil celulosa.

Una clase preferida de polímeros sintéticos incluye poliéteres tales como los óxidos de polialquileno. Típicamente, estos son polímeros con unidades repetidas de

oxialquileno en la columna del polímero. Entre los óxidos polialquilenos particularmente apropiados se incluyen los óxidos de polietileno y los óxidos de polipropileno. Generalmente estos polímeros tendrán un peso molecular de al menos 500.000 y a menudo al menos un millón. El peso molecular de los poliéteres puede ser hasta 15 millones o 20 millones o superior.

Otra clase preferida de polímeros sintéticos incluye los polímeros con adición de vinilo. Estos polímeros se forman de un monómero etilénicamente insaturado soluble en agua, o de una mezcla de monómeros.

El polímero soluble en agua puede ser catiónico, no iónico, anfotérico o aniónico. Los polímeros se pueden formar con cualesquiera monómeros adecuados solubles en agua. Típicamente los monómeros solubles en agua tienen una solubilidad en agua de al menos 5g/100cc a 25°C. Los polímeros aniónicos particularmente preferidos se forman de monómeros seleccionados de ácido carboxílico etilénicamente insaturado y monómeros de ácido sulfónico, preferiblemente escogidos de ácido metacrílico, ácido alil sulfónico y ácido 2-acrilamida-2-metil propanosulfónico y sus sales, opcionalmente en combinación con co-monómeros no iónicos, preferiblemente escogidos de metacrilamida, hidroxialquil ésteres de ácido metacrílico y N vinil pirrolidona. Los polímeros especialmente preferidos incluyen en homopolímero de acrilato de sodio, el homopolímero de acrilamida y el copolímero de acrilato de sodio con acrilamida.

Los polímeros no iónicos preferidos se forman de monómeros etilénicamente insaturados seleccionados de metacrilamida, hidroxialquil ésteres de ácido metacrílico y N vinil pirolidona.

Los polímeros catiónicos preferidos se forman de monómeros etilénicamente insaturados escogidos de dimetil amino etil metacrilato - metil cloruro (DMAEA Meci) quat, cloruro de dialil dimetil amonio (DADMAC), cloruro de trimetil amino propil metacrilamida (ATPAC), opcionalmente en combinación con comonómeros no iónicos, preferiblemente escogidos de metacrilamida, hidroxialquil ésteres de ácido metacrílico y N vinil pirolidona.

En la invención, el polímero puede formarse por cualquier proceso apropiado de polimerización. Los polímeros se pueden preparar por ejemplo como polímeros en gel por polimerización en solución, polimerización en suspensión de agua en aceite o por polimerización en emulsión de agua en aceite. Cuando se preparen polímeros en gel por polimerización en solución los iniciadores son introducidos generalmente en la solución de monómeros.

Opcionalmente puede incluirse un sistema de iniciador térmico. Típicamente un iniciador térmico incluiría cualquier compuesto iniciador adecuado que libere radicales a una temperatura elevada, por ejemplo compuestos azo, tales como azobis(isobutironitrilo). La temperatura durante la polimerización debe aumentarse al menos hasta 70°C, pero preferiblemente por debajo de 95°C. Alternativamente puede efectuarse la polimerización por radiación (luz ultravioleta, energía microondas, calor, etc.) usando también opcionalmente iniciadores apropiados de radiación. Una vez se completa la polimerización y el gel de polímero se ha enfriado lo suficiente el gel puede ser procesado en la forma estándar pulverizándolo primero en pedazos pequeños secándolo hasta formar un polímero sustancialmente deshidratado y finalmente moliéndolo en polvo.

Tales geles de polímero se pueden preparar por técnicas apropiadas de polimerización según se describen atrás, por

ejemplo por irradiación. Los geles pueden ser cortados a un tamaño adecuado según se requiera, y luego al aplicarlos se mezclan con el material como partículas de polímero soluble parcialmente hidratadas en agua.

Los polímeros se pueden producir como gotas por polimerización suspensión o como emulsión de agua en aceite o por dispersión por polimerización por emulsión de agua en aceite, por ejemplo según el proceso definido por EP-A-150933, EP-A-102760 o EP- A-126528.

Alternativamente el polímero soluble en agua puede proporcionarse como una dispersión en un medio acuoso. Esta puede por ejemplo ser una dispersión de partículas de polímero de al menos 20 micrones en un medio acuoso que contenga un agente equilibrante como aparece en EP-A-170394.

Este puede por ejemplo incluir también dispersiones acuosas de partículas de polímero preparadas por polimerización de monómeros acuosos en la presencia de un medio acuoso que contenga polímeros IV bajo disueltos, tales como cloruro de amonio de poli dialil-dimetilo, y opcionalmente otros materiales disueltos como por ejemplo compuestos de electrolitos y/o multihidroxilo como por ejemplo polialquilen glicoles, como se aprecia en WO-A-9831749 or WO-A-9831748.
La solución acuosa de polímero soluble en agua se obtiene típicamente disolviendo el polímero en agua o diluyendo una solución del polímero más concentrada. Generalmente polímero sólido particulado, por ejemplo en la forma de polvo o gotas, se dispersa en agua y se agita hasta que se disuelve. Esto se puede lograr usando un equipo convencional de producción. Deseablemente, el polímero en solución puede prepararse usando la marca Auto Jet Wet vendido por Ciba Specialty Chemicals. Alternativamente, el polímero puede ser proporcionado en forma de una emulsión o dispersión de fase inversa, que puede luego convertirse en agua.

Los siguientes ejemplos indican formas en las que puede emplearse la invención, sin que de ninguna manera puedan considerarse limitativas.

Ejemplos

Floculantes empleados

Descripción de los Polímeros usados

Polímero A - Un poliacrilato de sodio de aprox. 15.000.000 de peso molecular

Polímero B - Un homopolímero acrilamida de aprox. 5.000.000 de peso molecular

Polímero C - Un copolímero de sal de sodio de ácido acrilamido metil propan sulfónico/acrilamida de aprox. 15.000.000 de peso molecular

Polímero D - Copolímero de Acrilato de sodio / acrilamida 10/90 de aprox. 15,000,000 de peso molecular.

Polímero E - Copolímero de acrilato de sodio/acrilamida 30/70 de aprox. 15,000,000 de peso molecular.

Polímero F - Copolímero de acrilato de sodio/acrilamida 50/50 de aprox. 20,000,000 de peso molecular.

Polímero G - Copolímero de acrilato de sodio/acrilamida 30/70 de aprox. 17,000,000 de peso molecular.

Polímero H - Copolímero de metil cloruro dimetilaminoetilacrilato quaternario/acrilamida 60/40 de aprox. 12,000,000 de peso molecular.

Ejemplo 1.

Evaluación del efecto del Peróxido de Hidrógeno en la lechada de caolín

Procedimiento Experimental de Laboratorio

Se emplearon dos reproducciones exactas de lechada de caolín (50%p/p) para valorar el efecto del peróxido de hidrógeno sobre lechadas de caolín equivalentes no floculadas.

La primera lechada (muestra de control) se trató con agua ($1.5cm^3$). La segunda lechada fue tratada con Peróxido de Hidrógeno (30%) en una dosificación equivalente a 1500ppm (es decir, $1.5cm^3$). Se mezclaron estas adiciones a mano usando una espátula y se dejaron por un período de aproximadamente 30 minutos para que se estabilizaran. En esta coyuntura, el límite de fluencia de la lechada se midió usando un probador (tester) Brookfield de sólidos suaves (Aspa Media). Se tomaron varias lecturas del límite de fluencia en un período de tiempo.

El límite de fluencia se mide mediante el Reómetro Brookfield R/S SST en una temperatura ambiente de laboratorio de 25°C usando el programa de software RHEO V2.7 en un modo de Tasa de Corte Controlado. La rotación de una Veleta spindal (veleta 50_25 a un tamaño de tanque de 3 a 1) en pasos de 120 incrementos iguales de 0.025 rpm generan una aplicación progresiva de Tasa de Corte incrementada.

El límite de fluencia se define como el máximo esfuerzo cortante antes del inicio del corte. El límite de fluencia se calcula por regresión lineal de los 4 puntos de medición con Tasa de Corte > 0.1 1/s y el cálculo posterior de la interceptación del eje de Tau (Pa) para Tasa de Corte=0.
El trabajo anterior se realizó para confirmar si el peróxido de hidrógeno había tenido alguna interacción con la lechada no floculada. El requisito principal era demostrar que cualquier desviación del control se podría atribuir sólo a las interacciones floculantes.

Antes del tratamiento el límite de fluencia de la muestra de control era 334Pa en tanto que la muestra en espera del peróxido de hidrógeno tenía un límite de fluencia de 319Pa. El tratamiento con agua y peróxido de hidrógeno condujo a una reducción inmediata del límite de fluencia en la prueba de

control a 290Pa y con un registro de la prueba tratada con peróxido de hidrógeno de 284Pa.
Después de 89 horas el límite de fluencia de la muestra de control era de 244Pa en tanto que el sistema de peróxido de hidrógeno era de 203Pa.

En esta coyuntura, la dosificación de peróxido de hidrógeno se había incrementado a 15.000ppm para reflejar la dosificación más alta usada en las evaluaciones combinadas de subflujo que seguían, en tanto que el control era nuevamente sometido a un volumen equivalente de agua para anular los efectos de dilución. El límite de fluencia del control bajó a 185Pa en tanto que el sistema tratado bajó a 162Pa.

Después de 239 horas acumuladas, o 148 horas luego del incremento de la dosificación, la medida del límite de fluencia final de la muestra de control fue de 352Pa en tanto que el sistema tratado con peróxido de hidrógeno dio un límite de fluencia de 377Pa.

Estos resultados no se consideran significativamente diferentes e implican que no hay interacción entre la lechada de caolín y el peróxido de hidrógeno.

Ejemplo 2

La influencia del peróxido de hidrógeno sobre el volumen compacto y la reología del lecho sedimentado para una suspensión floculada de arcilla.

Procedimiento Experimental de Laboratorio

Se prepararon lechadas de caolín (6% p/v, 2g/l salteado) al granel. Se aplicaron soluciones del floculante escogido como una solución 0.05% p/p diluida de una solución original almacenada de 0.5% p/p. Se realizaron pruebas de floculación en 500 ml midiendo cilindros usando un método de agitación en

tanque. Se emplearon pruebas iniciales para establecer un perfil de dosificación inicial e identificar la dosificación necesaria requerida para lograr una tasa de sedimentación de 10 a 15 cm/min. Identificada la dosificación apropiada, se realizó un número de pruebas repetidas (dependiendo del número requerido de subflujos). Las lechadas tratadas se dejaron sedimentar a un nivel deseado, designado desde el comienzo de la prueba.

El licor sobrenadante se succionó hasta el nivel designado en cada cilindro requerido. Se adelantó una prueba de control combinando un número de subflujos en un cilindro de 1000ml con base removible, en ausencia de un tratamiento adicional. Las pruebas restantes requirieron el mismo número de subflujos combinados, aunque antes cada subflujo fue transferido a un cilindro de 1000ml y tratado con la dosificación dividida apropiada (es decir, una división de la dosificación total entre el número de subflujos a ser combinados) de peróxido de hidrógeno. Luego de combinar el número apropiado de subflujos, el cilindro fue llenado hasta 1000cm^3 con el líquido flotante removido anteriormente por succión.

En esta coyuntura se situaron rastrillos en cada cilindro, amarrados a motores (6rph) y alineados para asegurarse que se nivelaran y no fueran a ser obstruidos por las paredes del cilindro, y garantizar así un barrido consistente. Al comienzo de la activación del motor/barrido se anotó a intervalos el volumen de subflujo hasta que el subfluljo combinado se hubiera sedimentado a un nivel deseado o se hubiera compactado completamente hasta el nivel mínimo alcanzable. Logrado esto el líquido flotante se extrajo mediante succión a ~300cm^3 y los rastrillos fueron suavemente removidos. Entonces se removió la base para proporcionar una muestra reposada del lecho sedimentado. El límite de fluencia se midió usando un probador (tester) Brookfield de sólidos

suaves (Aspa Media), y terminada la medida reológica el subflujo se caracterizó, en términos de contenido sólido (%p/v y %p/p) porque secó una porción pesada.

Tabla 1 - Efecto del Floculante y el H_2O_2 en el límite de fluencia del subflujo

Límite de fluencia (Pa) contra contenido de sólidos (%p/v)

Contenido de sólidos, %p/v	Línea de Base	Polímero A	Polímero A con H_2O_2	Polímero B	Polímero B con H_2O_2
20.4	11				
22.2	14				
24.7	19				
26.1	22				
27.5	27				
29.3	34				
30.7	38				
31.4			20		
31.9		38			
32			21		
33	48				
33.3	53				
34		54			

34.7	62				
35.7		80			
37.4	103				
39.2	123				
39.9		162			
41			18		
41.1			10		
41.6	158				
42.9	184				
49.1		701			
50.1					54
50.8				584	

Los resultados para los Polímeros A y B se determinan en una gráfica según se muestra en la Figura 1.

La gráfica muestra que el uso de floculantes de alto peso molecular tiende a causar un incremento en el límite de fluencia del lecho sedimentado más allá del obtenido en el sustrato no tratado. La introducción del peróxido de hidrógeno al proceso de floculación ha resultado en una reducción del límite de fluencia en concentraciones sólidas

equivalentes a niveles significativamente inferiores que aquellos obtenidos en el material no tratado.

El Ejemplo 1 mostró que el Peróxido de Hidrogeno no reduce de manera independiente el límite de fluencia de la lechada de caolín, y por tanto las diferencias en un sistema floculado pueden atribuirse a la interacción sinergística entre los floculantes y el Peróxido de Hidrógeno.

De los resultados se infiere que el contenido de sólidos tiene un impacto reducido en el incremento del límite de fluencia comparado con la muestra de control no tratada, cuando el floculante presente en el subflujo, independientemente del contenido iónico, ha sido tratado con peróxido de hidrógeno.

Procedimiento Experimental de Laboratorio para los siguientes Ejemplos 3 - 9

Floculación inicial, pruebas de subflujo combinado / tratamiento químico y barrido seguidas de los métodos trazados en el laboratorio en el Ejemplo 3. Efecto de las dosificaciones de peróxido de hidrógeno en lechos sedimentados y reología.

Tabla 2 Influencia del Peróxido de Hidrógeno en las características de los lechos sedimentados de la floculación por Polímero A por 6%p/v (2g/1 salteado) de caolín

Características del lecho sedimentado	Control (0 ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno, ppm		
		15,000	1500	150

Sólidos, %p/p	36.5	40.0	40.5	43.0
Sólidos, %p/v	49.1	52.4	54.1	59.5
Límite de fluencia (Yield Stress), Pa	701.0	24.0	42.0	91.0

Una reducción de la dosificación de peróxido de hidrógeno parece promover el incremento en el contenido de sólidos con peróxido de hidrógeno, proporcionando 52.4, 54.1 y 59.5%p/v sólidos a 15.000, 1500 y 150ppm respectivamente. La dosificación más baja de peróxido de hidrógeno (150ppm) se equipara a un incremento en el contenido de subflujo de sólidos de 21% cuando se compara directamente con el control.

La medición del límite de fluencia del control es 701 Pa. El tratamiento con 15.000ppm de peróxido de hidrógeno reduce el límite de fluencia medido en aproximadamente 96% a 24Pa. 1500 y 150ppm de peróxido de hidrógeno reducen el límite de fluencia a 42Pa (reducción del 94%) y 91 Pa (reducción del 87%) respectivamente. De estos resultados se infiere que el límite de fluencia se reduce aún con contenidos incrementados de sólidos cuando el Polímero A floculante presente en el subflujo ha sido tratado con peróxido de hidrógeno.

Ejemplo 4

Tabla 3 Influencia del Peróxido de Hidrógeno en las características del lecho sedimentado por floculación por Polímero B a 6%p/v (2g/1 salteado) de caolín

Características del lecho	Control (0ppm Peróxido de	Peróxido de hidrógeno, ppm		
		15,000	1500	150

sedimentado	Hidrógeno)			
Sólidos, %p/p	42.6	42.2	43.0	43.1
Sólidos, %p/v	57.3	58.3	62.8	64.9
Límite de fluencia (Yield Stress), Pa	790.0	86.0	137.0	312.0

El peróxido de hidrógeno proporciona 58.3, 62.8 y 64.9%p/v sólidos a 15.000, 1500 y 150ppm respectivamente. La dosificación más baja de peróxido de hidrógeno (150ppm) se equipara a un incremento en el contenido de subflujo de sólidos de 13% cuando se compara directamente con el control.

La medición del límite de fluencia del control es 790 Pa. El tratamiento con 15.000ppm de peróxido de hidrógeno reduce el límite de fluencia medido en aproximadamente 89% a 86Pa. 1500 y 150ppm de peróxido de hidrógeno reducen el límite de fluencia a 137Pa (reducción del 83%) y 312Pa (reducción del 60%) respectivamente.

De estos resultados se infiere que el límite de fluencia se reduce aún con contenidos incrementados de sólidos cuando el Polímero B floculante presente en el subflujo ha sido tratado con peróxido de hidrógeno.

Ejemplo 5

Tabla 4 Influencia del Peróxido de Hidrógeno en las características del lecho sedimentado por floculación por Polímero B a 6%p/v (2g/1 salteado) de caolín

Características del lecho sedimentado	Control (0ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno, ppm		
		15,000	1500	150
Sólidos, %p/p	41.1	44.1	43.1	42.6
Sólidos, %p/v	57.1	62.0	59.8	63.3
Límite de fluencia (Yield Stress), Pa	761.0	157.0	142.0	209.0

El peróxido de hidrógeno proporciona 62.0, 59.8 y 63.3%p/v sólidos a 15.000, 1500 y 150ppm respectivamente. La dosificación más baja de peróxido de hidrógeno (150ppm) se equipara a un incremento en el contenido de subflujo de sólidos de 11% cuando se compara directamente con el control.

La medición del límite de fluencia del control es 761 Pa. El tratamiento con 15.000ppm de peróxido de hidrógeno reduce el límite de fluencia medido en aproximadamente 79% a 157Pa. 1500 y 150ppm de peróxido de hidrógeno reducen el límite de fluencia a 142Pa (reducción del 81%) y 209Pa (reducción del 72%) respectivamente.

De estos resultados se infiere que una mejora exitosa en relación con el control es posible por el uso de peróxido de hidrógeno con el Polímero C. A medida que la dosificación se reduce hay un incremento en el límite de fluencia subyacente, si bien los resultados se mantienen muy por debajo en relación con los del control aún con un contenido de sólidos más alto.

Ejemplo 6

Tabla 5 Influencia del Peróxido de Hidrógeno en las características del lecho sedimentado por floculación por Polímero D a 6%p/v (2g/1 salteado) de caolín

Características del lecho sedimentado	Control (0ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno, ppm			
		15,000	1500	150	15
Sólidos, %p/p	40.1	40.2	41.7	41.7	42.3
Sólidos, %p/v	51.9	54.9	56.4	56.7	64.4
Límite de fluencia (Yield Stress), Pa	804	66	87	91	219

El peróxido de hidrógeno proporciona 54.9, 56.4, 56.7 y 64.4%p/v sólidos a 15.000, 1500, y 15ppm respectivamente. La dosificación más baja de peróxido de hidrógeno (15ppm) se equipara a un incremento en el contenido de subflujo de sólidos de 24% cuando se compara directamente con el control.

La medición del límite de fluencia del control es 804 Pa. El tratamiento con 15.000ppm de peróxido de hidrógeno reduce el límite de fluencia medido en aproximadamente 92% a 66Pa. 1500, 150 y 15ppm de peróxido de hidrógeno reducen el límite de fluencia a 87Pa (reducción del 89%), 91Pa (reducción de 88%) y 219Pa (reducción del 73%) respectivamente.

De estos resultados se infiere que el límite de fluencia se reduce aún con contenidos de sólidos mayor cuando el floculante de Polímero D presente en el subflujo ha sido tratado con peróxido de hidrógeno, aún con la dosificación más baja empleada (15ppm).

Ejemplo 7

Tabla 6 Influencia del Peróxido de Hidrógeno en las características del lecho sedimentado por floculación por Polímero D a 4.6%p/v de residuos de lechada de carbón

Características del lecho sedimentado	Control (0ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno, ppm		
		15,000	1500	150
Sólidos, %p/p	49.8	49.7	50.8	50.9
Sólidos, %p/v	67.2	67.3	71.8	72.3
Límite de fluencia (Yield Stress), Pa	1139.0	13.0	243.0	221.0

El peróxido de hidrógeno proporciona 67.3, 71.8 y 72.3%p/v sólidos a 15.000, 1500 y 150ppm respectivamente. La dosificación más baja de peróxido de hidrógeno (150ppm) se equipara a un incremento en el contenido de subflujo de sólidos de 8% cuando se compara directamente con el control, y la dosificación de 1500 proporciona un incremento del 7%. En la dosificación más alta de peróxido de hidrógeno (15.000ppm), el subflujo de sólidos era equivalente al control.

La medición del límite de fluencia del control es 1139 Pa. El tratamiento con 15.000ppm de peróxido de hidrógeno reduce el límite de fluencia medido en aproximadamente 99% a 13Pa para un subflujo con contenido de sólidos semejante. 1500 y 150ppm de peróxido de hidrógeno reducen el límite de fluencia a 243Pa (reducción del 78%) y 221Pa (reducción del 80%) respectivamente.

De estos resultados se infiere que es posible una mejora exitosa en relación con el control por el uso de peróxido de hidrógeno con el Polímero D en residuos de carbón. A medida que la dosificación se reduce hay un incremento en el límite de fluencia subyacente, si bien los resultados se mantienen muy por debajo en relación con los del control.

Ejemplo 8

Tabla 7 Influencia del Peróxido de Hidrógeno en las características del lecho sedimentado por floculación por Polímero E a 6%p/v (2g/1 salteado) de caolín

Características del lecho sedimentado	Control (0ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno, ppm					
		15,000	1500	150	15	1.5	0.15
Sólidos, %p/p	36.7	40.6	39.8	39.2	41.5	39.0	39.7
Sólidos, %p/v	51.2	55.4	55.2	53.3	58.6	53.5	55.4
Límite de fluencia (Yield Stress),Pa	540	78	76	65	116	117	353

El peróxido de hidrógeno proporciona 55.4, 55.2, 53.3, 58.6, 53.5 y 55.4%p/v sólidos a 15.000, 1500, 15, 1.5 y 0.15ppm respectivamente. La dosificación de peróxido de hidrógeno de 15ppm se equipara a un incremento en el contenido de subflujo de sólidos de 14% cuando se compara directamente con el control.

La medición del límite de fluencia del control es 540Pa. El tratamiento con 15.000ppm de peróxido de hidrógeno reduce el

límite de fluencia medido en aproximadamente 86% a 78Pa. 1500, 150, 15, 1.5 y 0.15ppm de peróxido de hidrógeno reducen el límite de fluencia a 76Pa (reducción del 86%), 65Pa (reducción de 88%), 116Pa (reducción del 78%), 117Pa (reducción del 78%) y 353Pa (reducción del 35%) respectivamente.

De estos resultados se infiere que el límite de fluencia no se incrementa por el contenido aumentado de sólidos cuando el floculante de Polímero D presente en el subflujo ha sido tratado con peróxido de hidrógeno, aún con la baja dosificación de 1.5ppm.

Ejemplo 9

Tabla 8 Influencia del Peróxido de Hidrógeno en las características del lecho sedimentado por floculación por Polímero E a un 4.6%p/v de lechada de residuos de lavadura de Arena y Gravilla

Características del lecho sedimentado	Control (0ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno, ppm				
		15,000	1500	150	15	1.5
Sólidos, %p/p	35.9	30.0	36.5	37.6	34.5	37.3
Sólidos, %p/v	46.8	37.1	50.1	51.5	44.4	49.2
Límite de fluencia (Yield Stress), Pa	1187	51	337	877	867	1100

El peróxido de hidrógeno proporciona 37.1, 50.1, 51.5, 44.4 y 49.2%p/v sólidos a 15.000, 1500, 15 y 1.5ppm respectivamente.

A 15.000 y 15ppm esto se equipara a un decremento en el contenido de subflujo de sólidos de 21 y 5% respectivamente cuando se compara directamente con el control. El contenido de sólidos obtenido a 150ppm se equipara a un incremento del 10% cuando se compara directamente con el control.

La medición del límite de fluencia del control es 1187Pa. El tratamiento con 15.000ppm de peróxido de hidrógeno reduce el límite de fluencia medido en aproximadamente 95.7% a 51Pa aunque esto es con un contenido de sólidos reducido. 1500ppm de peróxido de hidrógeno reduce el límite de fluencia a 337Pa (reducción del 72%), lo cual es un decrecimiento significativo, en contenido de sólidos más altos. 150, 15 y 1.5ppm de peróxido de hidrógeno reduce el límite de fluencia a 887Pa (reducción del 26%), 867Pa (reducción del 27%) y 1100Pa (reducción del 7% respectivamente.

De estos resultados se infiere que se logra un exitoso incremento en el contenido de sólidos compactos en combinación con las reducciones en el límite de fluencia comparado con el control con el tratamiento del Polímero E con el uso combinado de peróxido de hidrógeno.

Ejemplo 10

Influencia de los oxidantes y otros reactivos en caolín floculado a 4% p/v (2g/1 salteado)

Para probar una amplia variedad de reactivos se diseñó una prueba de muestreo como sigue:

1. 675 ml de 4% p/v (2g/1 salteado) de caolín se en un bombona alta de 1000 ml. Se agitó el contenido a 400rpm usando un agitador mecánico. Se agregaron 225 ml de una solución diluida (aproximadamente 0.002% de agua deionizada) de Polímero E y se agitó continuamente por 4 minutos. Se redujo la velocidad de agitación a 200rpm por dos minutos

más. Luego se suspendió la agitación y se anotó el tiempo que tomó al lodo sedimentarse entre las marcas de 750ml y 550. La tasa de sedimentación en cm/min se calculó desde esta cifra.

2. De estas pruebas e estableció la dosificación de Polímero E requerida para alcanzar una tasa de sedimentación de alrededor de 10cm/min, evaluando un rango de concentraciones de la solución. Una vez esta dosificación se estableció, la misma dosificación se usó para las pruebas subsiguientes.

3. El procedimiento descrito bajo el número 1 se repitió, por la cual la solución diluida de Polímero E se preparó en agua deionizada, como un control. Una vez se midió la tasa de sedimentación inicial, se dejó la mezcla reposar por un período de tiempo y luego se agitó a 200 rpm por 2 minutos, y se midió de nuevo el tiempo de sedimentación. Esto se repitió varias veces por un período de varias horas.

4. Para evaluar los diferentes reactivos, éstos se agregaron a la solución de polímero antes de ser agregados al caolín en una cantidad que arrojó una dosificación de 1000ppm en la lechada final.

En los resultados en la Tabla 9 se anotó la tasa de sedimentación luego de que pasó un total de 18 horas de tiempo. Dentro de este período de tiempo cada muestra había sido agitada y se le dejó sedimentar un total de 3 veces.

La dosificación del Polímero E usada en todas las pruebas fue de 4.0 mg/l. La tasa de sedimentación del control a la hora cero era 9.8 cm/min.

Tabla 9

Reactivo	Tasa de sedimentación a 18 horas (cm/min)
Control	7.8
Peróxido de hidrógeno	0.6
Perborato de sodio	3.8
Hipoclorito de Sodio	0.6
Persulfato de Sodio	6.1
Metabisulfito de Sodio	4.0
Bisulfito de sodio	3.3
Persulfato de aluminio	1.8
Nitrito de Sodio	8.1
Nitrato de Sodio	8.1

Los reactivos que arrojaron una tasa de sedimentación significativamente menor que el control indican que la degradación del floculante o estructura de masa flotante ha tenido lugar a un mayor grado que cuando simplemente se usa agitación mecánica. En la tabla anterior todos los reactivos que se conocen como fuentes de agentes oxidantes/radicales libres mostraron una degradación del floculo a un grado mayor o menor.

Ejemplo 11

Tabla 10 Influencia de los reactivos oxidantes en caolín floculado al 4%p/v (pH 2 ajustado usando ácido sulfúrico).

Se pretende que este sustrato sea representativo de los capas encontradas en procesos hidrometalúrgicos que incluyen lixiviación de ácidos como por ejemplo cobre, zinc electrolítico, etc.

Se usó el procedimiento de la prueba descrita en el ejemplo 10 pero usando el Polímero B y 4% p/p de caolín ajustado a pH 2 como sustrato.

En los resultados que aparecen más abajo se anotó la tasa de sedimentación después de un total de 21 horas de tiempo. Dentro de este período de tiempo cada muestra había sido agitada y se le dejó sedimentar por un total de 4 veces.

La dosificación del Polímero B usada en todas las pruebas era 18 mh/l la tasa de sedimentación del control a la hora cero era 9.3.cm/min.

En esta serie de pruebas un rango de niveles de dosificación de los reactivos se agregó tal como se indica en la tabla más abajo.

Reactivo	Dosificación (ppm)	Tasa de sedimentación a 21 horas de tiempo transcurrido
Control	-	9.3
Peróxido de hidrógeno	100	0.7
	350	0.6
	600	0.5
	1000	0.5

Perborato de Sodio	100	0.6
	350	0.7
	600	0.6
	1000	0.6
Hipoclorito de Sodio	100	3.1
	350	6.9
	600	3.1
	1000	3.2

Los 3 reactivos mostraron una degradación de los flóculos durante el período de tiempo investigado.

Ejemplo 12

Tabla 11 Influencia del peróxido de hidrógeno en caolín floculado al 4%p/v (conteniendo 33.3g/l de hidróxido de sodio).

Se pretende que este sustrato sea representativo de los capas encontradas en procesos hidrometalúrgicos que incluyen lixiviación de álcalis como por ejemplo alúmina, u otros sistemas alcalinos.

Se usó el procedimiento de la prueba descrita en el ejemplo 11 pero usando el Polímero F y 4% p/p de caolín conteniendo 33.3g/l de hidróxido de sodio como sustrato de prueba.

En los resultados que aparecen más abajo se anotó la tasa de sedimentación después de un total de 21 y 66 horas de tiempo. Dentro de este período de tiempo cada muestra había sido agitada y se le dejó sedimentar por un total de 3 veces por 21 horas y 5 x por 66 horas. La dosificación del Polímero F usada en todas las pruebas era de 3.3 mg/l. La tasa de sedimentación del control a la hora cero era 9.3 cm/min.

Dosificación de Peróxido de Hidrogeno	Tasa de sedimentación a 21 horas de tiempo transcurrido	Tasa de sedimentación a 66 horas de tiempo transcurrido
Control	10.2	6.9
100	7.6	8.1
350	11.3	14.6
600	11.2	10.9
1000	8.8	9.4

Bajo estas condiciones el peróxido de hidrógeno es ineficaz, lo que indica que será necesario un rango de reactivos para diferentes circunstancias.

Ejemplo 13

Tabla 12 Influencia del Hipoclorito de Sodio y el Perborato de Sodio en caolín floculado al 4%p/v (conteniendo 33.3g/l de hidróxido de sodio).

Se usó el procedimiento de la prueba descrita en el ejemplo 13 pero usando el Polímero F y 4% p/p de caolín conteniendo 33.3g/l de hidróxido de sodio como sustrato de prueba.

En los resultados que aparecen más abajo se anotó la tasa de sedimentación después de un total de 26 horas y 90 horas de tiempo. Dentro de este período de tiempo cada muestra había sido agitada y se le dejó sedimentar por un total de 3 veces por 26 horas y 4 x por 90 horas. La dosificación del Polímero F usada en todas las pruebas era de 3.3 mg/l. La tasa de sedimentación del control a la hora cero era 9.6 cm/min.

Reactivo	Dosificación del Reactivo	Tasa de sedimentación a 21 horas de tiempo transcurrido	Tasa de sedimentación a 66 horas de tiempo transcurrido
	Control	10.2	7.7
Hipoclorito de Sodio	100	8.9	5.2
	350	9.6	4.4
	600	7.3	No se tomaron resultados
	1000	4.3	1.5
Perborato de Sodio	100	15	5.5
	350	6.3	5.5
	600	12.7	5.3
	1000	11.7	4.2

Ambos reactivos alcanzaron degradación luego de un largo período de tiempo.

Ejemplo 14

Tabla 13 La influencia del Peróxido de Hidrógeno en residuos de una operación de extracción de granito.

Se usó el procedimiento de la prueba descrita en el ejemplo 13 pero usando el Polímero G y residuos de operaciones de extracción de granito a sólidos de 3% p/v como sustrato de prueba.

En los resultados más abajo se anotó la tasa de sedimentación después de un total de 20 horas de tiempo. Dentro de este período de tiempo cada muestra había sido agitada y se le dejó sedimentar por un total de 6 veces. La dosificación del Polímero G usada en todas las pruebas era de 1.5 mg/l. La tasa de sedimentación del control a la hora cero era 8.2 cm/min.

Dosificación de Peróxido de Hidrógeno (ppm)	Tasa de sedimentación a 20 Horas tiempo transcurrido
Control	6.4
1	6.9
5	5.2
10	3.9
100	3.0
500	0.8

Estos resultados mostraron que el peróxido de hidrógeno causa degradación de las masas flotantes que se forman en este efluente, pero se requiere al menos 5ppm para que pueda tener algún efecto y los mejores resultados de obtienen a >100ppm.

Ejemplo 15

Tabla 14 La influencia del Peróxido de Hidrógeno en las características de la floculación con Polímero G de lechos sedimentados con residuos de una operación de extracción de granito.

Se usó el procedimiento de la prueba descrita en el ejemplo 2 con la excepción de que se usaron los residuos de una operación de extracción de granito a sólidos de 3% en lugar de la lechada de caolín y se usó el Polímero G para flocular la muestra a un nivel de dosificación de 1.5. mg/.

Características del lecho sedimentado	Control (0ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno (ppm)		
		10	100	500
Contenido de sólidos % (p/p)	46.9	44.3	46.6	47.4
Límite de fluencia (Yield Stress) (Pa)	99	10	29	4

Estos resultados muestran que el límite de fluencia del subflujo es significativamente inferior que el de la muestra de control con un contenido de sólidos similar. También confirma que las pruebas descritas en el Ejemplo 14 proporcionan una buena indicación de los reactivos que afectan benéficamente las características del subflujo.

Ejemplo 16

Tabla 15 La influencia del Peróxido de Hidrógeno en las características de los lechos sedimentados de Polímero D. Carboximetil Celulosa (CMC) y mezclas de polímero 0044 y la floculación CMC de 16%p/v (2g/l salteado) de caolín

Se usó el procedimiento de la prueba descrita en el ejemplo 2. Debido a las capacidades de floculación diferentes del CMC y el Polímero D, se requirieron niveles diferentes de dosificaciones de los polímeros individuales y las mezclas para alcanzar el nivel apropiado de floculación.

Características del lecho sedimentado	Control (0ppm Peróxido de Hidrógeno)	Peróxido de hidrógeno (ppm)			
		15	150	1500	15000
Floculado utilizando 11.5 mg/l Polímero D					
Contenido de sólidos % (p/p)	40.1	42.3	41.7	41.7	40.2
Límite de fluencia (Yield Stress) (Pa)	804	219	91	87	66
Floculado utilizando 50mg/l CMC					
Contenido de sólidos % (p/p)	38.7	38.3	37.7	36.5	36.4
Límite de fluencia (Yield Stress) (Pa)	718	187	19	11	17
Floculado utilizando 20 mg/l 80:20 Polímero D:CMC					
Contenido de sólidos % (p/p)	38.7	39.0	39.8	39.9	38.6
Límite de fluencia (Yield Stress) (Pa)	510	179	163	113	62

Estos resultados muestran que se obtuvieron modestos incrementos en el contenido de los subflujos de sólidos por la adición de peróxido de hidrógeno cuando se realizó la floculación usando el Polímero D y mezclas de Polímero D y CMC. No se observó incremento en los subflujos de sólidos cuando se realizó la floculación usando solamente CMC. Sin

embargo, para todos los tratamientos de floculación la adición de peróxido de hidrógeno proporciona una significativa reducción en el límite de fluencia de entre 72% y 97%.

Ejemplo 17

Tabla 16 La influencia del peróxido de hidrógeno en caolín a 4% (2g/l salteado) floculado con un floculante catiónico - Polímero H. Se realizaron pruebas según se describe en el Ejemplo 10, excepto que se usó el Polímero H como floculante, se estableció la dosis de 5cm/min a 8.8mg/l para alcanzar la tasa final de sedimentación, se midió la sedimentación final después de 27 horas y cada muestra se agitó y dejó sedimentar un total de 8 veces en este período. La tasa de sedimentación del control a la hora cero era de 4.4 cm/min.

Reactivo	Tasa de sedimentación a 27 horas (cm/min)
Control	5.8
Peróxido de hidrógeno	2.1
Perborato de Sodio	<1
Hiperclorito de Sodio	<1

Ejemplo 18

Tabla 17 La influencia del agua de Ozono en caolín a 4% (2g/l salteado) floculado con el Polímero D

Se realizaron pruebas como sigue: Se colocaron 800 mls de lechada de caolín a 4% (2g/l salteados) en un cilindro de 1000ml. La lechada se agitó mecánicamente usando un agitador de paletas rotando a 900rpm. 20 mls de una solución de 0.05% de Polímero D se agregaron al sustrato y se batieron por 50

segundos. La tasa resultante de sedimentación libre de los sólidos de lodo se midió.*[1] Una vez los sólidos se sedimentaron por debajo de la marca de 250 ml los contenidos del cilindro se batieron por 15 segundos y se midió de nuevo la tasa de sedimentación libre. Esto se repitió las veces que fueron necesarias. Cuando se usó ozono la prueba se repitió al punto *[1]. Luego el ozono se convirtió en burbujas en la muestra a una tasa de 31/minuto por 15 minutos. El generador de ozono se apagó y toda la muestra se agitó a 900 rpm durante 15 segundos y la tasa de sedimentación se midió de nuevo.

Prueba	Comentarios del tratamiento	Tasa de sedimentación horas (cm/min)
Control no floculante		0.14
Control - 20 mls of 0.05% Polímero D	Medición inicial	13.9
	Re-Agitado 1	9.1
	Re-Agitado 2	6.9
	Re-Agitado 3	5.6
	Re-Agitado 4	4.9
	Re-Agitado 5	4.4
20 mls 0.05% Polímero	Medición inicial	9.7
	Siguiendo tratamiento de ozono	0.41

Estos resultados muestran que la adición de ozono anula el efecto de la floculación a tal grado que la tasa de sedimentación se acerca al del caolín no floculado. La degradación mecánica por batido no se acerca a este efecto.

Ejemplo 19

La influencia del peróxido de hidrógeno en el peso molecular del Polímero E en solución.

Procedimiento

Se pesaron 27.82g de 100 volúmenes (30%p/v) de peróxido de hidrógeno en un frasco volumétrico de 250 ml para producir una solución al 33.3%. También se preparó una fase movible para cromatografía excluyente de tamaño de doble fuerza (SEC), 11.68g NaCl + 2.28g K_2HPO_4 en un frasco volumétrico de 500ml. Una solución de aproximadamente 0.5% de Polímero E se preparó en agua deionizada y se dejó durante la noche. Se midió el peso seco en un horno encendido a 110C. Una porción de la solución de polímero se pesó en un frasco volumétrico de 100 ml. Se agregaron 50 ml de amortiguador (fase movible SEC de doble fuerza) y la solución se diluyó hasta la marca con solución de peróxido de hidrógeno. Se preparó una muestra de control de manera similar, pero el agua deionizada se sustituyó por una solución de peróxido.

Se hicieron mediciones de un punto de viscosidad específica usando un viscómetro capilar Schott 531 10 Ubbelohde en una unidad de medida de viscosidad automática AVS 350.

Polímero E con Peróxido de Hidrógeno		Polímero E Control
Tiempo desde Inicio / mins	1 pt sp visc dl/g	1 pt sp visc dl/g
12	23.09	
35		22.78
66	23.02	
129	22.92	

152		22.74
215	22.77	

267		22.65
399	22.43	
412		22.50
1356	21.83	
1385	20.58	
4394		22.32
5786	14.63	

Esto indica que el peróxido de hidrógeno produce degradación del peso molecular del Polímero E

Reivindicaciones

1. Un proceso de concentrar de una suspensión acuosa de partículas sólidas que comprende los pasos de agregar al menos un floculante polimérico orgánico a la suspensión formando así sólidos floculados, en donde los sólidos floculados forman un sustrato de sólidos formando entonces una suspensión más concentrada, en donde el proceso comprende la adición de una cantidad efectiva de un agente que se selecciona de un grupo consistente en agentes radicales libres, agentes oxidantes, enzimas y radiación, donde el agente es aplicado a la suspensión antes o de manera sustancialmente simultánea con la adición del floculante polimérico orgánico y/o el floculante polimérico orgánico se agrega a la suspensión en un tanque y los agentes se aplican a la suspensión en el mismo tanque.

2. Un proceso de acuerdo con la reivindicación 1 en el que el agente se selecciona de perboratos, percarbonatos, arbonatos, persulfatos, ozono y peróxidos.

3. Un proceso de acuerdo con la reivindicación 1 o la reivindicación 2 en donde el agente es peróxido de hidrógeno.

4. Un proceso de acuerdo con cualquier reivindicación precedente en donde al agente causa la fragmentación de la estructura floculada.

5. Un proceso de acuerdo con cualquier reivindicación precedente en donde el agente causa la degradación del floculante polimérico orgánico.

6. Un proceso de acuerdo con cualquier reivindicación precedente en donde el agente causa una reducción en el límite de fluencia del sustrato de sólidos hasta al menos 30% por debajo del límite de fluencia de un sustrato de sólidos a

un contenido equivalente de sólidos sin la adición del agente.

7. Un proceso de acuerdo con cualquier reivindicación precedente en donde la adición del agente causa un incremento en el contenido de sólidos de al menos 5% en peso del sustrato teniendo un límite de fluencia dado en comparación con un sustrato que tenga el mismo límite de fluencia de un proceso equivalente, pero con la ausencia del agente.

8. Un proceso de acuerdo con cualquier reivindicación precedente en donde el agente desarrolla un gas.

9. Un proceso de acuerdo con cualquier reivindicación precedente en donde los sólidos floculados forman un lecho y se libera agua de la suspensión, y en donde el tratamiento del lecho de sólidos por el agente causa un incremento en el contenido de sólidos del lecho en comparación con un proceso equivalente realizado en la ausencia del agente.

10. Un proceso de acuerdo con cualquier reivindicación precedente en donde los sólidos floculados se sedimentan para formar un lecho de sólidos y se libera agua de la suspensión, y en donde el agente está en contacto con el lecho y dicho agente desarrolla burbujas de gas que causan la formación de canales en tal lecho y facilita la liberación de agua de la suspensión.

11. Un proceso de acuerdo con cualquier reivindicación precedente en donde la suspensión se somete a floculación en un tanque de sedimentación gravimétrico o área de desecho y los sólidos floculados se dejan decantar por sedimentación y forman una sustrato compacto de sólidos más concentrados.

12. Un proceso de acuerdo con cualquier reivindicación precedente en donde el sustrato de sólidos forma un subflujo, el cual es entonces transferido a un área de desecho.

13. Un proceso de acuerdo con cualquier reivindicación precedente en donde la suspensión acuosa comprende partículas minerales.

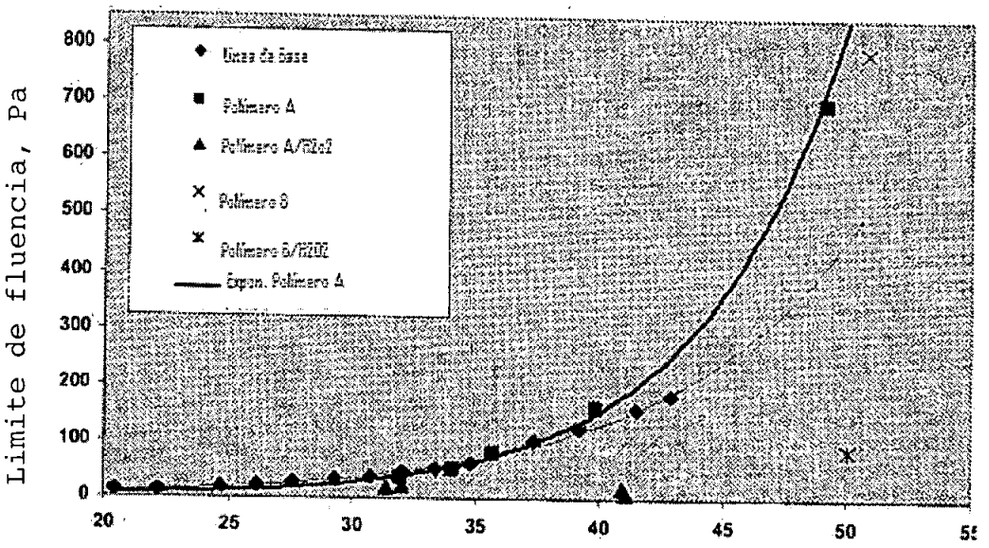
14. Un proceso de acuerdo con cualquier reivindicación precedente en donde la suspensión acuosa se deriva de operaciones de procesamiento de minerales o energía y/o capas de residuos y se selecciona de un grupo consistente de bauxita, metales base, metales preciosos, hierro, níquel, carbón, arenas minerales, arenas de aceite, caolín, diamantes y uranio.

15. Un proceso de acuerdo con cualquier reivindicación precedente en donde el floculante polimérico orgánico es un polímero no iónico o aniónico que es bien sea un polímero sintético de viscosidad intrínseca de al menos 4 dl/g o un polímero natural.

16. Un proceso de acuerdo con cualquier reivindicación precedente en donde el floculante polimérico orgánico se selecciona de un grupo consistente en un homopolímero de acrilato de sodio, el homopolímero de acrilamida y el copolímero de acrilamida y acrilato de sodio.

FIGURA 1

Límite de fluencia vs Contenido de Sólidos (% p/v)



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(54) Title: CONCENTRATION OF SUSPENSIONS

(57) Abstract: The present invention relates to a process of concentrating an aqueous suspension of solid particles comprising the steps of adding at least one organic polymeric flocculant to the suspension thereby forming flocculated solids in which the flocculated solids are allowed form a layer of solids and thereby forming a more concentrated suspension in which the process comprises the addition of an effective amount of an agent that is selected from the group consisting of free radical agents, oxidising agents, enzymes and radiation, in which the agent is applied to the suspension prior to or substantially simultaneously with adding the organic polymeric flocculant and/or the organic polymeric flocculant is added to the suspension in a vessel and the agent is applied to the suspension in the same vessel. The process is particularly suitable for solids liquid separation in which the flocculated solids are allowed to settle by sedimentation in a gravity thickener.

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Concentration of Suspensions

The present invention relates to an improved flocculation process for the concentration of suspensions. In particular flocculated solids can be settled to form a bed in which higher solids and/or reduced yield stress can be achieved.

It is known to concentrate suspensions of solids in aqueous liquids by use of flocculants resulting in flocculation of the solids which facilitates the separation of the solids from the liquid. In many processes the flocculated solids settle to form a bed by sedimentation. In other processes separation can be facilitated by mechanical dewatering, for instance in pressure filtration, centrifugation, by belt thickeners and belt presses.

The types of flocculant added to the suspension will often depend upon the substrate. Generally suspensions tend to be flocculated by high molecular weight polymers. Examples of this are described in WO-A-9314852 and US3975496 regarding the flocculation of mineral suspensions such as red mud. Other disclosures of high molecular weight polymeric flocculants include US 6447687, WO-A-0216495 and WO-A-02083258 dealing with the flocculation of sewage sludge. It is known to sometimes add other chemical additives to condition the suspension. For instance suspensions may be first coagulated by a high charged density polymeric coagulant such as polyDADMAC or inorganic coagulants including ferric chloride.

Other additives are also use in conditioning of suspensions. For example peroxides are sometimes added to suspensions such as sewage sludges or other suspensions containing organic material in order to remove reducing agents in order to reduced odours, gas formation or prevent putrefaction. In general the peroxides or oxidising agents tend to be added in order to remove harmful or unwanted substances or other materials contained in the suspension.

Generally the amount of peroxides added is only sufficient to remove the unwanted substances and materials and generally peroxides or other oxidising agents are included in relatively small amounts.

Examples of adding peroxides to sewage sludge are described in JP56150481. Peroxides or oxidising agents may also be added to other suspensions for similar reasons including treating dredged material to remove contaminants as described in US 2003 121863 and JP 10109100. JP 11156397 describes a process for flocculating mud using non-ionic and anionic polymers in which the mud has been pretreated with an oxidising agent.

U.S. 6733674 describes a method of dewatering sludge by adding an effective amount of one or more cellulolytic enzymes and one or more oxidants and one or more flocculants to form a mixture in water which is coagulated and flocculated followed by separation of solids from the water. The examples seem to indicate a significant time elapsed between oxidant addition and flocculation. The enzymes appeared to be present in order to degrade material contained in the sludge.

Suspensions are frequently concentrated in a gravity thickener vessel. A continual flow of the suspension is typically fed into the thickener and treated with a flocculant. The flocculated solids thus formed settle to form a bed of solid underflow and supernatant aqueous liquid flows upwards and is usually removed from the thickener vessel through a perimeter trough at the water surface. Normally the thickener vessel has a conical base such that the underflow can easily be removed from the centre of the base. In addition a rotating rake assists the removal of the underflow solids. A typical process for concentrating suspensions in a gravity thickener is described in US4226714.

Various suspensions can be concentrated in gravity thickeners, including suspensions of organic solids such as wastewater, sewage and sewage

sludges. If it also commonplace to thicken or dewater mineral suspensions using gravity thickeners.

In a typical mineral processing operation, waste solids are separated from solids that contains mineral values in an aqueous process. The aqueous suspension of waste solids often contain clays and other minerals, and are usually referred to as tailings. These solids are often concentrated by a flocculation process in a thickener and settle to form a bed. Generally it is desirable to remove as much water from the solids or bed in order to give a higher density underflow and to recover a maximum of the process water. It is usual to pump the underflow to a surface holding area, often referred to as a tailings pit or dam, or alternatively the underflow may be mechanically dewatered further by, for example, vacuum filtration, pressure filtration or centrifugation.

US 5685900 describes a selective flocculation process for beneficiating a low brightness fine particle size kaolin in order to reduce a higher brightness kaolin clay. The process involves a classification step to recover the kaolin fraction wherein the particles are at least 90% by weight below 0.5μm. The recovered fraction is then subjected to a bleaching step to partially bleach organic discolorants. The resulting slurry is selectively flocculated using a high molecular weight anionic polyacrylamide or acrylate acrylamide copolymer. This flocculation step forms a supernatant phase which is highly concentrated with contaminant titania and a flocced clay phase which is devoid of titania that contains the discolorants. The flocs are then treated with gaseous ozone in order to oxidising the remaining discolouring organics and also destroy the flocculant polymer in order to restore the kaolin to a dispersed state. This is said to be achieved by passing the flocculated solids through an ozonation step, preferably using a high shear pump.

Similar disclosures are made in WO 2004 071 989 and US 2006 0131243.

WO 2005 021129 discloses controlling the condition of a suspension of solid particles within a liquid including applying 1 or more stimuli to the suspension. In this disclosure conditioning is preferably reversible and involves flocculation and/or coagulation in which inter particle forces may be attractive or repulsive between the solid particles within the liquid. The stimulus may be one or more chemical additives and may for instance be a stimulus sensitive polyelectrolyte which can be absorbed on the surface of the suspended particles in sufficient quantity to create steric or electrostatic repulsion between the particles. In one instance a polyelectrolyte may be substantially insoluble at pH values where it is substantially uncharged thereby to effect flocculation of the suspension. Polyelectrolytes that are responsive to a temperature stimulus are also described. Reference is also given to a method of controlling the consolidation of a bed of solid particles within a liquid by applying one or more stimuli to the bed. Each or the stimulus effects reversibly operable conditioning between an initial state prevailing prior to said applying one or more stimuli and a conditioning state resultant from said one or more stimuli. The processes described bring about improvements in certain solids liquids separation activities.

JP 11-46541 describes a temperature sensitive hydrophilic polymer added to a suspension of particles below a transition temperature whereupon flocs are formed by absorbing and cross-linking particles as a conventional flocculant. The mixture is heated to above the transition temperature and the absorbed polymer becomes hydrophobic and the suspended particles are rendered hydrophobic and form flocs by hydrophobic interaction. Appropriate external pressure is applied at this time and the particles are readily realigned and water between the particles is expelled by the hydrophobicity of the particles.

JP 2001 232104 describes a process similar to JP 11-46541 but using improved temperature sensitive flocculants that are ionic temperature sensitive polymer as opposed to non-ionic polymers which a absorb onto suspended particles and

when the polymer becomes hydrophobic at temperatures about the transition point there are strong hydrate layers around the ionic groups but hydrated layer adhesion between the polymers is prevented by hydrophobic interaction.

Bertini, V.et. al. Particulate Science and Technology (1991), 9(3-4), 191-9 describes the use of multifunctional polymers for the pH controlled flocculation of titanium minerals. The polymers are radical vinyl copolymers containing catechol functions and acrylic acid units. The polymers can change their effect from flocculating to dispersing or inert and vice versa by changing pH.

The pH or temperature sensitive flocculants in principle provide control over the flocculation state of a suspension. However, the choice of flocculant would need to be appropriate for the particular suspension or bed that is to be flocculated and at the same time be responsive to a particular stimulus to bring about the reversibly operable conditioning. In some cases it may be difficult to find the right choice of flocculant.

Frequently some water will be trapped in the flocculated solids and this water is often difficult to release and therefore held in the bed. Whilst pH and temperature responsive flocculants may assist with this problem it is often difficult to achieve satisfactory flocculation across a wide range of substrates.

In processes involving gravity thickeners it is desirable to operate such that the bed has the highest possible solids capable of being removed from the thickener as an underflow. Normally the limiting factor is the ability of the rake in the thickener to move the sedimented solids. It would therefore be desirable to provide a process which increases the rate of separation of the solids from the suspension and removal of the underflow.

According to the present invention we provide a process of concentrating an aqueous suspension of solid particles comprising the steps of adding at least

one organic polymeric flocculant to the suspension thereby forming flocculated solids in which the flocculated solids are allowed form a layer of solids and thereby forming a more concentrated suspension in which the process comprises the addition of an effective amount of an agent is selected from the group consisting of free radical agents, oxidising agents, enzymes and radiation,
in which the agent is applied to the suspension prior to or substantially simultaneously with adding the organic polymeric flocculant and/or
the organic polymeric flocculant is added to the suspension in a vessel and the agent is applied to the suspension in the same vessel.

We have found that inclusion of the agent significantly improves the efficiency of the concentration process. By concentration we mean that the solids content of the suspension is increased. Typically concentration of a suspension will include dewatering processes and thickening processes and the like.

Preferably the flocculated solids are allowed to settle to form a bed of solids which may also be termed a sediment. More preferably the process involves sedimentation in a gravity thickener and a sediment or bed is removed from the thickener as an underflow.

Surprisingly contacting the layer or bed of solids with the agent enables a significant increase in aqueous liquid released.

Desirably the agent brings about fragmentation of the flocculated structure. Preferably, we find that the flocculated network can collapse and often occupy a small volume than the settled solids would have occupied in the absence of the agent.

In one form the agent may bring about degradation of the organic polymeric flocculant. It is believed that the chemical interaction between the flocculant and

the solids is permanently altered as a result of this degradation of polymeric flocculant. The polymer may be degraded such that the solids have a reduced flocculated network. In one aspect the polymer chain may break down into smaller chains which induces a dispersant effect on the solids. In some cases the polymer may be degraded to the extent that it no longer has a flocculating effect on the solids. The degradation of the organic polymeric flocculant preferably is in conjunction with a degradation or size reduction of the flocculated structure. In a more preferred form we find that the flocculated network collapses thereby increasing the solids content for a given volume.

In one preferred form the agent brings about a reduction in the yield stress of a layer of solids formed from the action of the organic flocculant. More preferably the layer of solids should be at least 30% below the yield stress of a layer of solids at an equivalent solids content without the addition of the agent. Thus the agent desirably brings about a reduction in the yield stress of the layer or bed of solids it enables higher solids to be achieved and an increased removal of the underflow. Preferably the reduction in yield stress will be at least 50% below the yield stress of a layer of solids at an equivalent solids content without the addition of the agent. More preferably the reduction in yield stress will be at least 60 or 70% and often at the least 80 or 90%.

Unexpectedly we have also found that the stress can be reduced below the yield stress of a layer of solids at an equivalent solids content that had not been flocculated and without the addition of the agent. Until now it has been a generally accepted view that sedimentation of solids in the absence of flocculation would achieve the lowest yield stress. It was generally believed that a process involving flocculation would always result in a higher yield stress than in the absence of the flocculant because the flocculant would tend to hold the sedimented solids in a structure that would tend to increase the yield stress. Consequently it is particularly surprising that such a process involving the use of

the flocculant may result in a yield stress below the yield stress than a settled suspension without the use of flocculant.

Preferably the above-mentioned reductions in yield stress will be in combination with either a degradation or fragmentation of the flocculated structure and/or alternatively in combination with a degradation of the organic polymeric flocculant. It is especially preferred that the degradation of the organic polymeric flocculant is responsible for a degradation or size reduction of the flocculated structure which in turn brings about a reduction of the yield stress of the layer or bed of solids.

In a preferred form of the process the flocculated solids settle to form a bed and water is released from the suspension and in which we have found that the exposure of the flocculated solids to the agent brings about an increase in the water released from the suspension. Consequently, we find that this increase in water released is also accompanied by an increase in the solids.

In a further aspect the agent may evolve a gas. We find that the release of gas into the layer or bed of solids can enhance the release of water. In a preferred form the flocculated solids settle to form a bed and the agent is in contact with the flocculated solids or the bed and this brings about a further release of for and an increase in the solids. Preferably, the gas is released and forms gas bubbles. Without being limited to theory it is believed that the gas may for instance cause the formation of channels or fissures in the bed of solids and facilitate the release of water from the suspension.

Agents that can evolve a gas include carbonates, bicarbonates and peroxides.

The process of the present invention has been found to enhance the concentration of a suspension, especially by gravity sedimentation. In this sense the rate of consolidation of separated solids is increased. In addition the

mobility of concentrated phase, i.e. settled or sedimented solids, can be significantly improved.

The agent may be one or more chemical compounds selected from the group consisting of free radical agents, oxidising agents and enzymes. Alternatively or additionally when the agent brings about degradation or fragmentation of the flocculated structure and/or degradation of the organic polymeric flocculant and/or brings about a reduction in the yield stress of the layer or bed solids the agent may also include radiation. The radiation may be for instance ultrasound, ionising radiation or electromagnetic radiation. When the agent evolves gas it may alternatively be a mechanical apparatus that releases gas bubbles from within the layer of solids, especially where the layer is a sediment or bed.

The agent is preferably selected from the group consisting of free radical agents, oxidising agents and enzymes.

It has been found that the incorporation of a free radical agent or oxidising agent into the flocculation process has resulted in a more rapid compaction phase, and/or reduced viscosity of the layer or bed of solids e.g. sediment at corresponding solids contents such that a higher solids content can be achieved without exceeding the maximum viscosity that the equipment carrying out the removal process can tolerate. In further embodiment enzymes have also been found to provide a similar effect. This is particular the case when the polymer is a natural polymer or semi natural polymer, for instance polysaccharide which may have been modified, and the selected enzyme is known to degrade the natural or semi natural polymer.

Suitable free radical agents include chemical compounds selected from the group consisting off ferrous ammonium sulphate, ceric ammonium nitrate etc.

It may also be desirable to use activators in conjunction with the free radical agents which in some cases may accelerate the radical generation. Typically

such activators include amino carboxylates and diamines, cupric EDTA (ethylene diamine tetra acetic acid) and reducing sugars such as fructose and lactose.

Any conventional oxidising agent may be used. Oxidising agents may be chemical substances selected from the group consisting of chlorine, transition metal or other metal compounds in a high oxidation state, such as chromium, manganese, iron and copper compounds each of which include substances that are powerful oxidizing agents, tBHP (tertiary butyl hydro peroxide), sodium sulphite , bi-sulphite compounds, ammonium per sulphate, sodium perborate, sodium hypopchlorite and ozone.

The use of ozone, peracetic, perborates, percarbonate and persulphates have been found to be particularly effective for oxidizing purposes.

Any suitable enzyme capable of acting on the organic polymeric flocculant, particularly as a natural polymer, may be used. Typically such enzymes include hydrolases. Suitable enzymes include proteases, which will break down proteins; glycosylases which break down sugars; pectinases which break down pectin; amylases which degrade starch; esterases which degrade any ester bonds; cellulases which break down cellulose and cellulose compounds; glucosidases and galactosidases or degrading sugars. Other hydrolases may modify the surface of other polymeric flocculants, including for instance polyamides and polyesters. Other enzymes include depolymerases which will break down a polymer, particularly microbiologically generated polymers such as polyesters. Preferred enzymes include amylases, cellulases, galactomannanases. In general these are suitable for use with natural or semi natural polymers for example starch, CMC (carboxy methyl cellulose), guar, alginates, pectinates and sulphated gum carrageenan. Other specific enzymes are known to act on chitosan.

Preferred agents for use in present invention are peroxides. A particular preferred peroxide is hydrogen peroxide.

In the process the agent and the organic polymeric flocculant may be added to the suspension sequentially or simultaneously. Some operations may work better if the agent is added subsequent to the polymeric flocculant. This may be especially so if the agent acts relatively quickly since sufficient time must be allowed to first substantially form the flocculated structure before any substantial effects of the agent occur. Nevertheless, with this order of addition the organic polymeric flocculant should be added to the suspension in a vessel and the agent is applied to the suspension in the same vessel. In this case it is preferred that the agent is added into the layer or bed of solids. Typically this vessel may be a thickener, for instance a gravity thickener used for the sedimentation of suspended solids.

However, in many situations it is preferred that the agent is applied to the suspension prior to or substantially simultaneously with adding the organic polymeric flocculant. Without being limited theory it is thought that adding the agent before any substantial formation of the flocculant structure will ensure that the agent is distributed throughout the flocculated solids. Addition of the agent and the flocculant simultaneously may also provide the advantage of a single addition point especially if the agent and the flocculant are premixed. However, with mixtures of agent and flocculant it may be necessary to ensure that the mixture is applied to the suspension prior to any significant deleterious effects of the agent on the flocculant.

The agent should be applied in an effective amount. Preferably a sufficient quantity should be added in order to ensure that it brings about at least one of:
i) fragmentation of the flocculated structure; and/or
ii) degradation of the organic polymeric flocculant; and/or

iii) brings about a reduction in the yield stress of the layer of solids below the yield stress of a layer of solids at an equivalent solids content that had not been flocculated and without the addition of the agent and/or;

iv) enables an increase in the solids content of at least 5% by weight of the layer having a given yield stress compared to a layer having the same yield stress from an equivalent process but in the absence of the agent.

The amount of agent will vary according to the specific process conditions, the type of substrate and flocculant. The agent preferably should be present in an amount of at least 1 ppm based on weight of agent on volume of the suspension. The agent can be effective at low levels for example between 1 and 10 ppm. Generally the agent will be added in an amount of from at least 100 ppm and in some cases may be at least 1000 ppm based on the weight of the solids in the suspension. In some cases it may be desirable to add significantly higher levels of the agent, for instance as much as 40,000 or 50,000 ppm or higher. Effective doses usually will be in the range between 150 and 20,000 ppm, especially between 1000 and 15,000 ppm.

More preferably the increase in water released from the layer or bed and the increased solids of the layer or bed is also accompanied by a decrease in yield stress. Preferably we find that the yield stress of the layer or bed is less than a layer or bed at equivalent solids content in which the flocculated solids are not exposed to the agent.

It is known that in general solids in suspensions will often settle without the addition of flocculant. The flocculant brings about bridging flocculation of the solids and increases the rate at which the solids settle to form a bed. Thus in conventional gravity thickening situations, improved rate of free settlement and initial compaction are achieved by the use of polymeric flocculants and optionally coagulants. In such a process the individual solid particles tend to gather together to form aggregates which have a more favourable density to

surface area ratio. These aggregates can settle to form a compacted bed from which water can be further removed by upward percolation. In this way the bed progressively increases in solids content over an extensive period of time until the desired solids concentration in the bed is reached and material in the bed can be removed.

Unfortunately, in general the viscosity or yield stress of the flocculated settled solids in conventional processes tends to be significantly higher than the settled solids in the absence of the flocculant. This tends to make the removal process of raking and pumping progressively more difficult. On the other hand it would not be practical to concentrate a suspension in the absence of flocculant since this would take an extremely long time, especially in a gravimetric thickener which relies upon free sedimentation.

In the process according to the invention we have found that a more rapid compaction phase can be achieved. In addition it has been found that the present process tends to result in a significantly reduced viscosity or yield stress of the layer of solids or bed as a result of treatment by the agent. In particular we find that the yield stress is not only lower than the equivalent process in the absence of the agent, but the yield stress can be as low as or lower than settled solids in the absence of the flocculant. In some cases we find that the process results in a layer or bed of solids having a yield stress significantly below that of settled solids in the absence of flocculant. This unexpected property of the settled solids facilitates the ease of removal of a solids underflow whilst at the same time ensuring rapid settling of the solids. Furthermore, it is preferred that the process is operated by allowing the solids content of the consolidated bed to increase significantly above that which can be tolerated by the equipment in the absence of the agent. In this sense the consolidated bed may still be operated at the maximum yield stress for the equipment but in which the solids content is significantly higher than the bed in a process without the agent.

The yield stress of the layer of solids including sedimented bed will vary according to the substrate. Typically the maximum yield stress of a sedimented bed that can be tolerated by conventional equipment is usually no more than 250 Pa. Within capabilities of the existing equipment it would not be possible to increase the solids using the conventional process since the yield stress would be too high. The process of the invention employing the agent has been found to reduce the yield stress by at least 10% and usually at least 50% and in some cases as much as 80 or 90% or higher. On the other hand the solids content of the layer or bed produced according to the invention can be allowed to increase by at least 5% and sometimes more than 10% without exceeding the maximum yield stress that can be tolerated by the equipment. In some cases it may be possible to increase the solids by up to 15 or 20% or more in comparison to a layer or bed having the same yield stress obtaining by the equivalent process but in the absence of the agent.

The actual weight percent underflow solids that can be achieved with acceptable yield stress varies considerably dependent upon the constituent and particle size of the suspended solids, and also the age and sophistication of the settling equipment. It may be as low as around 12% (typically Florida phosphate slimes) but is usually between around 20% and 50%.

The Yield Stress is measured by Brookfield R/S SST Rheometer at an ambient laboratory temperature of 25°C using the RHEO V2.7 software programme in a Controlled Shear Rate mode. Rotation of a Vane spindal (50_25 vane at a 3 to 1 vessel sizing) in 120 equal step increases of 0.025 rpm generate a progressive application of increased Shear Rate.

Yield Stress is defined as the maximum shear stress before the onset of shear. The Yield Stress is calculated by linear regression of the 4 measurement points with Shear Rate > 0.1 1/s and subsequent calculation of the intercept of the axis of Tau (Pa) for Shear Rate = 0.

The invention is applicable to any solids liquid separation activity in which solids are separated from a suspension. This may include for instance processes involving sedimentation, centrifugation, pressure filtration, belt pressing or belt thickening. The invention is of particular benefit to sedimentation processes. Particularly preferred processes involve subjecting the suspension to flocculation in a gravimetric thickener. In such a process the solids form a compacted layer of concentrated solids, which in general will be significantly higher than in the absence of the agent.

The flocculated solids resulting from the process may form an underflow which may be removed from the flocculation and settling zone. In many instances flocculated solids form an underflow which is then transferred to a disposal area.

As indicated previously the invention is applicable generally to solids liquid separation processes. Thus the suspension may comprise organic material including for instance sewage sludge or cellular material from fermentation processes. The suspension may also be a suspension of cellulosic material, for instance sludges from papermaking processes. Preferably the suspension is an aqueous suspension comprising mineral particles.

In a more preferred aspect of the invention the process involves the treatment of aqueous suspensions resulting from mined mineral processing and other mining wastes, for instance from carbon based industries such as coal and tar sands, comprising suspensions of mineral particles, especially clays. Thus in this preferred aspect of the process the aqueous suspension is derived from mineral or energy processing operations and/or tailings substrates. By energy processing operations we mean preferably processes in which the substrate involves the separation of materials useful as fuels.

A particularly preferred aspect of the process involves suspensions selected from mining and refining operations the group consisting of bauxite, base metals, precious metals, iron, nickel, coal, mineral sands, oil sands, china clay, diamonds and uranium.

Preferably suspended solids in the suspension should be at least 90% by weight greater than 0.5 microns. Frequently the particles in suspension will be at least 90% by weight at least 0.75 microns and preferably at least 90% by weight at least one or two microns. Typically suspended particles may have a particle size at least 90% by weight up to 2mm and usually at least 90% by weight within the range above 0.5 microns to 2 mm. Preferably suspended particles will be at least 90% by weight up to 1 mm or more preferably at least 90% by weight up to 750 microns, especially at least 90% by weight within the range of between one or two microns and one or two millimetres.

The suspensions will often contain at least 5% by weight suspended solids particles and may contain as much as 30% or higher. Preferably suspensions will contain at least 0.25% more preferably at least 0.5% Usually the suspensions will contain between 1% and 20% by weight suspended solids.

Suitable doses of organic polymeric flocculant range from 5 grams to 10,000 grams per tonne of material solids. Generally the appropriate dose can vary according to the particular material and material solids content. Preferred doses are in the range 10 to 3,000 grams per tonne, especially between 10 and 1000 grams per tonne, while more preferred doses are in the range of from 60 to 200 or 400 grams per tonne.

The aqueous polymer solution may be added in any suitable concentration. It may be desirable to employ a relatively concentrated solution, for instance up to 10 % or more based on weight of polymer. Usually though it will be desirable to add the polymer solution at a lower concentration to minimise problems

resulting from the high viscosity of the polymer solution and to facilitate distribution of the polymer throughout the suspension. The polymer solution can be added at a relatively dilute concentration, for instance as low as 0.01% by weight of polymer. Typically the polymer solution will normally be used at a concentration between 0.05 and 5% by weight of polymer. Preferably the polymer concentration will be the range 0.1% to 2 or 3%. More preferably the concentration will range from 0.25% to about 1 or 1.5%. Alternatively the organic polymeric flocculant may be added to the suspension in the form of dry particles or instead as a reverse phase emulsion or dispersion. The dry polymer particles would dissolve in the aqueous suspension and the reverse phase emulsion or dispersion should invert directly into the aqueous suspension into which the polymer would then dissolve.

The process according to the invention exhibits improved sedimentation rates. It has been found that sedimentation rate is between 2 and 30 m/hour can be achieved. In addition we find that the process enables greater than 99% by weight of the suspended solids to be removed from a suspension. In addition the process enables an increase in solids sediment concentrations of greater than 10% by weight in comparison to conventional processes operating in the absence of the agent. More preferably reduced sediment yield stress is obtaining compared to the best conventional processes.

The organic polymeric flocculant may include high molecular weight polymers that are cationic, non-ionic, anionic or amphoteric. Typically if the polymer is synthetic it should exhibit an intrinsic viscosity of at least 4 dl/g. Preferably though, the polymer will have significantly higher intrinsic viscosity. For instance the intrinsic viscosity may be as high as 25 or 30 dl/g or higher. Typically the intrinsic viscosity will be at least 7 and usually at least 10 or 12 dl/g and could be as high as 18 or 20 dl/g.

Intrinsic viscosity of polymers may be determined by preparing an aqueous solution of the polymer (0.5-1% w/w) based on the active content of the polymer. 2 g of this 0.5-1% polymer solution is diluted to 100 ml in a volumetric flask with 50 ml of 2M sodium chloride solution that is buffered to pH 7.0 (using 1.56 g sodium dihydrogen phosphate and 32.26 g disodium hydrogen phosphate per litre of deionised water) and the whole is diluted to the 100 ml mark with deionised water. The intrinsic viscosity of the polymers are measured using a Number 1 suspended level viscometer at 25°C in 1M buffered salt solution.

Alternatively, the organic polymeric flocculant may be a natural polymer or semi natural polymer. Typical natural or semi natural polymers include polysaccharides. This will include cationic starch, anionic starch, amphoteric starch, chitosan.

One preferred class of polymers includes for instance polysaccharides such as starch, guar gum or dextran, or a semi-natural polymer such as carboxymethyl cellulose or hydroxyethyl cellulose.

One preferred class of synthetic polymers includes polyethers such as polyalkylene oxides. Typically these are polymers with alkylene oxy repeating units in the polymer backbone. Particularly suitable polyalkylene oxides include polyethylene oxides and polypropylene oxides. Generally these polymers will have a molecular weight of at least 500,000 and often at least one million. The molecular weight of the polyethers may be as high as 15 million of 20 million or higher.

Another preferred class of synthetic polymers include vinyl addition polymers. These polymers are formed from an ethylenically unsaturated water-soluble monomer or blend of monomers.

The water soluble polymer may be cationic, non-ionic, amphoteric, or anionic. The polymers may be formed from any suitable water-soluble monomers. Typically the water soluble monomers have a solubility in water of at least 5g/100cc at 25°C. Particularly preferred anionic polymers are formed from monomers selected from ethylenically unsaturated carboxylic acid and sulphonic acid monomers, preferably selected from (meth) acrylic acid, allyl sulphonic acid and 2-acrylamido-2-methyl propane sulphonic acid, and their salts, optionally in combination with non-ionic co-monomers, preferably selected from (meth) acrylamide, hydroxy alkyl esters of (meth) acrylic acid and N-vinyl pyrrolidone. Especially preferred polymers include the homopolymer of sodium acrylate, the homopolymer of acrylamide and the copolymer of sodium acrylate with acrylamide.

Preferred non-ionic polymers are formed from ethylenically unsaturated monomers selected from (meth) acrylamide, hydroxy alkyl esters of (meth) acrylic acid and N-vinyl pyrrolidone.

Preferred cationic polymers are formed from ethylenically unsaturated monomers selected from dimethyl amino ethyl (meth) acrylate - methyl chloride, (DMAEA.MeCl) quat, diallyl dimethyl ammonium chloride (DADMAC), trimethyl amino propyl (meth) acrylamide chloride (ATPAC) optionally in combination with non-ionic co-monomers, preferably selected from (meth) acrylamide, hydroxy alkyl esters of (meth) acrylic acid and N-vinyl pyrrolidone.

In the invention, the polymer may be formed by any suitable polymerisation process. The polymers may be prepared for instance as gel polymers by solution polymerisation, water-in-oil suspension polymerisation or by water-in-oil emulsion polymerisation. When preparing gel polymers by solution polymerisation the initiators are generally introduced into the monomer solution.

Optionally a thermal initiator system may be included. Typically a thermal initiator would include any suitable initiator compound that releases radicals at an elevated temperature, for instance azo compounds, such as azo-bis-isobutyronitrile. The temperature during polymerisation should rise to at least 70°C but preferably below 95°C. Alternatively polymerisation may be effected by irradiation (ultra violet light, microwave energy, heat etc.) optionally also using suitable radiation initiators. Once the polymerisation is complete and the polymer gel has been allowed to cool sufficiently the gel can be processed in a standard way by first comminuting the gel into smaller pieces, drying to the substantially dehydrated polymer followed by grinding to a powder.

Such polymer gels may be prepared by suitable polymerisation techniques as described above, for instance by irradiation. The gels may be chopped to an appropriate size as required and then on application mixed with the material as partially hydrated water soluble polymer particles.

The polymers may be produced as beads by suspension polymerisation or as a water-in-oil emulsion or dispersion by water-in-oil emulsion polymerisation, for example according to a process defined by EP-A-150933, EP-A-102760 or EP-A-126528.

Alternatively the water soluble polymer may be provided as a dispersion in an aqueous medium. This may for instance be a dispersion of polymer particles of at least 20 microns in an aqueous medium containing an equilibrating agent as given in EP-A-170394. This may for example also include aqueous dispersions of polymer particles prepared by the polymerisation of aqueous monomers in the presence of an aqueous medium containing dissolved low IV polymers such as poly diallyl dimethyl ammonium chloride and optionally other dissolved materials for instance electrolyte and/or multi-hydroxy compounds e. g. polyalkylene glycols, as given in WO-A-9831749 or WO-A-9831748.

The aqueous solution of water-soluble polymer is typically obtained by dissolving the polymer in water or by diluting a more concentrated solution of the polymer. Generally solid particulate polymer, for instance in the form of powder or beads, is dispersed in water and allowed to dissolve with agitation. This may be achieved using conventional make up equipment. Desirably, the polymer solution can be prepared using the Auto Jet Wet (trademark) supplied by Ciba Specialty Chemicals. Alternatively, the polymer may be supplied in the form of a reverse phase emulsion or dispersion which can then be inverted into water.

The following examples indicate ways in which the invention can be employed without in any way intending to be limiting.

Examples

Flocculants employed

Description of Polymers used

Polymer A - a sodium polyacrylate of approx 15,000,000 molecular weight

Polymer B – an acrylamide homopolymer of approx 15,000,000 molecular weight

Polymer C – a sodium salt of acrylamido methyl propane sulphonic acid/ acrylamide copolymer of approx. 15,000,000 molecular weight.

Polymer D – sodium acrylate /acrylamide 10/90 copolymer of approx 15,000,000 molecular weight.

Polymer E - sodium acrylate /acrylamide 30/70 copolymer of approx 15,000,000 molecular weight.

Polymer F - sodium acrylate /acrylamide 50/50 copolymer of approx 20,000,000 molecular weight.

Polymer G - sodium acrylate /acrylamide 30/70 copolymer of approx 17,000,000 molecular weight.

Polymer H – methyl chloride quaternised dimethylaminoethylacrylate /acrylamide 60/40 copolymer of approx 12,000,000 molecular weight.

Example 1.

Evaluation of Hydrogen Peroxide Effect on China Clay Slurry

Laboratory Experimental Procedure

Two replicate china clay slurries, (50 %w/w), were employed to assess the effect of hydrogen peroxide on equivalent non-flocculated china clay slurries. The first slurry (control sample) were treated with water ($1.5cm^3$). The second slurry was treated with Hydrogen Peroxide (30%) at a dose equivalent to 1500ppm (ie $1.5cm^3$). These additions were mixed by hand using a spatula and left for a period of 30 minutes to stabilise. At this juncture, the yield stress of the

slurry was measured using a Brookfield soft solids tester (Medium Vane). A number of Yield Stress readings were taken over time.

The Yield Stress is measured by Brookfield R/S SST Rheometer at an ambient laboratory temperature of 25°C using the RHEO V2.7 software programme in a Controlled Shear Rate mode. Rotation of a Vane spindal (50_25 vane at a 3 to 1 vessel sizing) in 120 equal step increases of 0.025 rpm generate a progressive application of increased Shear Rate.

Yield Stress is defined as the maximum shear stress before the onset of shear. The Yield Stress is calculated by linear regression of the 4 measurement points with Shear Rate > 0.1 1/s and subsequent calculation of the intercept of the axis of Tau (Pa) for Shear Rate = 0.

The above work was conducted to confirm whether hydrogen peroxide had any interaction with the unflocculated slurry. The principle requisite is to prove that any deviation from the control could be attributable to flocculant interactions alone.

Prior to treatment the yield stress of the control sample was 334Pa whilst the sample awaiting hydrogen peroxide treatment had a yield stress of 319Pa. Treatment with water and hydrogen peroxide led to an immediate decline in yield stress with the control at 290Pa and the hydrogen peroxide treated test registering 284Pa.

After 89 hours the yield stress of the control sample was 244Pa whilst the hydrogen peroxide system was 203Pa.

At this juncture, the hydrogen peroxide dose was increased to 15,000ppm to reflect the higher dose used in the combined underflow evaluations that follow, whilst the control was again subject to an equivalent volume of water to negate

dilution effects. The yield stress of the control dropped to 185 Pa whilst the treated system fell to 162Pa.

After 239 cumulative hours, or 148 hours beyond the dose increase, final yield stress measurement for the control was 352Pa whilst the hydrogen peroxide treated system provided a yield stress of 377Pa.

These results are not deemed to be significantly different and imply that there is no interaction between the china clay slurry and the hydrogen peroxide.

Example 2

The influence of hydrogen peroxide on the compacted volume and settled bed rheology for a flocculated clay suspension

Laboratory Experimental Procedure

China clay slurries (6% w/v, 2g/l salted) were made up in bulk. Solutions of the chosen flocculant were applied as a 0.05% w/w solution diluted from a 0.5% w/w original stock solution. Flocculation tests were conducted in 500 ml measuring cylinders employing a plunger method of agitation. Initial tests were employed to establish a flocculant dose profile and identify the required dose necessary for attainment of a settlement rate of 10 to 15 cm/min. Upon identifying an appropriate dose, a number of repeat tests (dependent upon the required number of underflows) were carried out. The treated slurries were left to settle to a desired level, designated at the onset of testwork.

The supernatant liquor was siphoned of to the designated level in each cylinder required. A control test was progressed by combining a set number of underflows in a 1000ml cylinder with removable base, in the absence of any additional treatment. The remaining tests required the same number of combined underflows, however before each underflow was transferred to a 1000ml cylinder, it was treated with an appropriate split dose (ie total dose split

between the number of underflows to be combined) of hydrogen peroxide. Upon combining the appropriate number of underflows, the cylinder was topped up to 1000cm3 with the siphoned supernatant liquor, removed earlier.

At this juncture rakes were placed in each cylinder, attached to motors (6rph) and aligned to ensure they were level and not obstructed by the cylinder walls to ensure consistent raking. Upon commencement of motor activation/raking, the underflow volume was recorded at intervals, until the combined underflow had settled to a desired level or was fully compacted to its lowest attainable level. Upon completion the supernatant liquor was siphoned of to ~300cm^3 and the rakes were gently removed. The base was then removed to provide an undisturbed sample of the settled bed. The yield stress of the compacted underflow was measured using a Brookfield soft solids tester (Medium Vane) and upon completion of the rheology measurement the underflow was characterised in terms of solids content (%w/v and %w/w), by drying a weighed portion.

Table 1 Effect of flocculant and H_2O_2 on the underflow Yield Stress

Yield Stress (Pa) versus Solids Content (%w/v)

Solids Content, %w/V	Baseline	Polymer A	Polymer A with H_2O_2	Polymer B	Polymer B with H_2O_2
20.4	11				
22.2	14				
24.7	19				
26.1	22				
27.5	27				
29.3	34				
30.7	38				
31.4			20		
31.9		38			
32			21		

33	48				
33.3	53				
34		54			
34.7	62				
35.7		80			
37.4	103				
39.2	123				
39.9		162			
41			18		
41.1			10		
41.6	158				
42.9	184				
49.1		701			
50.1					54
50.8				584	

Results for Polymers A and B are plotted in a graph shown in Figure 1.

The graph shows that the use of high molecular weight flocculants tends to impart an increase in settled bed Yield Stress beyond that given by the untreated substrate. The introduction of hydrogen peroxide to the flocculation process has resulted in a reduction in Yield stresses, at equivalent solids concentrations, to levels significantly lower than those given by untreated material.

Example 1 showed that Hydrogen Peroxide does not independently reduce the Yield Stress of the china clay slurry, therefore, any differences in a flocculated system can be attributed to the synergistic interaction between flocculant and Hydrogen Peroxide.

Results infer that increased solids content has a reduced impact on increasing yield stress compared to the untreated control, when the flocculant present in the underflow, irrespective of ionic content, has undergone treatment via hydrogen peroxide.

Laboratory Experimental Procedure for the following Examples 3 - 9

Initial flocculation, combined underflow / chemical treatment and raking tests followed the methods outlined in the laboratory experimental procedure in

Example 3. Effect of hydrogen peroxide dose on settled bed compaction and rheology

Table 2 Influence of Hydrogen Peroxide on settled bed characteristics of Polymer A flocculation for 6%w/v (2g/l salted) China Clay

Settled Bed Characteristics	Control (0 ppm Hydrogen Peroxide)	Hydrogen Peroxide, ppm		
		15,000	1500	150
Solids, %w/w	36.5	40.0	40.5	43.0
Solids, %w/v	49.1	52.4	54.1	59.5
Yield Stress, Pa	701.0	24.0	42.0	91.0

A decrease in hydrogen peroxide dose appears to promote increased solids contents with hydrogen peroxide providing 52.4, 54.1 and 59.5%w/v solids at 15,000, 1500 and 150ppm respectively. The lowest hydrogen peroxide dose (150ppm) equates to an increase in underflow solids content of 21% when compared directly to the control.

The yield stress measurement of the control is 701Pa. Treatment with 15,000ppm hydrogen peroxide reduces the measured yield stress by approximately 96% to 24Pa. 1500 and 150ppm hydrogen peroxide reduces the yield stress to 42Pa (94% reduction) and 91Pa (87% reduction) respectively. These results infer that yield stress is reduced even at increased solids contents when Polymer A flocculant present in the underflow has undergone treatment via hydrogen peroxide.

Example 4

Table 3 Influence of Hydrogen Peroxide on settled bed characteristics of Polymer B flocculation for 6%w/v (2g/l salted) China Clay

Settled Bed Characteristics	Control (0 ppm Hydrogen Peroxide)	Hydrogen Peroxide, ppm		
		15,000	1500	150
Solids, %w/w	42.6	42.2	43.0	43.1
Solids, %w/v	57.3	58.3	62.8	64.9
Yield Stress, Pa	790.0	86.0	137.0	312.0

Hydrogen peroxide provides 58.3, 62.8 and 64.9%w/v solids at 15,000, 1500 and 150ppm respectively. The lowest hydrogen peroxide dose (150ppm) equates to an increase in underflow solids content of 13% when compared directly to the control.

The yield stress measurement of the control is 790Pa. Treatment with 15,000ppm hydrogen peroxide reduces the measured yield stress by approximately 89% to 86Pa. 1500 and 150ppm hydrogen peroxide reduces the yield stress to 137Pa (83% reduction) and 312Pa (60% reduction) respectively.

These results infer that yield stress is reduced even at increased solids contents when Polymer B flocculant present in the underflow has undergone treatment via hydrogen peroxide.

Example 5

Table 4 Influence of Hydrogen Peroxide on settled bed characteristics of Polymer C flocculation for 6%w/v (2g/l salted) China Clay

Settled Bed Characteristics	Control (0 ppm Hydrogen Peroxide)	Hydrogen Peroxide, ppm		
		15,000	1500	150
Solids, %w/w	41.1	44.1	43.1	42.6
Solids, %w/v	57.1	62.0	59.8	63.3
Yield Stress, Pa	761.0	157.0	142.0	209.0

Hydrogen peroxide provides 62.0, 59.8 and 63.3%w/v solids at 15,000, 1500 and 150ppm respectively. The lowest hydrogen peroxide dose (150ppm) equates to an increase in underflow solids content of 11% when compared directly to the control.

The yield stress measurement of the control is 761Pa. Treatment with 15,000ppm hydrogen peroxide reduces the measured yield stress by approximately 79% to 157Pa. 1500 and 150ppm hydrogen peroxide reduces the yield stress to 142Pa (81% reduction) and 209Pa (72% reduction) respectively. These results infer that successful improvement over the control is possible through the use of hydrogen peroxide with Polymer C. As the dose is reduced there is an increase in the underlying yield stress, however the results still remain well below that of the control even at higher solids contents.

Example 6.

Table 5 Influence of Hydrogen Peroxide on settled bed characteristics of Polymer D flocculation for 6%w/v (2g/l salted) China Clay

Settled Bed Characteristics	Control (0 ppm Hydrogen Peroxide)	Hydrogen Peroxide, ppm			
		15,000	1500	150	15
Solids, %w/w	40.1	40.2	41.7	41.7	42.3
Solids, %w/v	51.9	54.9	56.4	56.7	64.4
Yield Stress, Pa	804	66	87	91	219

Hydrogen peroxide provides 54.9, 56.4, 56.7 and 64.4%w/v solids at 15,000, 1500, 150 and 15ppm respectively. The lowest hydrogen peroxide dose (15ppm) equates to an increase in underflow solids content of 24% when compared directly to the control.

The yield stress measurement of the control is 804Pa. Treatment with 15,000ppm hydrogen peroxide reduces the measured yield stress by approximately 92% to 66Pa. 1500, 150 and 15ppm hydrogen peroxide reduces the yield stress to 87Pa (89% reduction), 91Pa (88% reduction) and 219Pa (73% reduction) respectively.

These results infer that yield stress is reduced even at increased solids content when the Polymer D flocculant present in the underflow has undergone treatment via hydrogen peroxide, even at the lowest dose employed (15ppm).

Example 7.

Table 6 Influence of Hydrogen Peroxide on settled bed characteristics of Polymer D flocculation for a 4.6%w/v coal tailings slurry

Settled Bed Characteristics	Control (0 ppm Hydrogen Peroxide)	Hydrogen Peroxide, ppm		
		15,000	1500	150
Solids, %w/w	49.8	49.7	50.8	50.9
Solids, %w/v	67.2	67.3	71.8	72.3
Yield Stress, Pa	1139.0	13.0	243.0	221.0

Hydrogen peroxide provides 67.3, 71.8 and 72.3%w/v solids at 15,000, 1500 and 150ppm respectively. The lowest hydrogen peroxide dose (150ppm) equates to an increase in underflow solids content of 8% when compared directly to the control, and the 1500 ppm dose gives a 7% increase. At the highest hydrogen peroxide dose (15,000ppm), the underflow solids were equivalent to the control.

The yield stress measurement of the control is 1139Pa. Treatment with 15,000ppm hydrogen peroxide reduces the measured yield stress by approximately 99% to 13Pa for an underflow with similar solids content. 1500 and 150ppm hydrogen peroxide reduces the yield stress to 243Pa (78% reduction) and 221Pa (80% reduction) respectively.

These results infer that successful improvement over the control is possible through the use of hydrogen peroxide with Polymer D on coal tailings. As the dose is reduced there is an increase in the underlying yield stress, however the results still remain well below that of the control.

Example 8.

Table 7 Influence of Hydrogen Peroxide on settled bed characteristics of Polymer E flocculation for 6%w/v (2g/l salted) China Clay

Settled Bed Characteristics	Control (0 ppm Hydrogen Peroxide)	Hydrogen Peroxide, ppm					
		15,000	1500	150	15	1.5	0.15
Solids, %w/w	36.7	40.6	39.8	39.2	41.5	39.0	39.7
Solids, %w/v	51.2	55.4	55.2	53.3	58.6	53.5	55.4
Yield Stress, Pa	540	78	76	65	116	117	353

Hydrogen peroxide provides 55.4, 55.2, 53.3, 58.6, 53.5 and 55.4%w/v solids at 15,000, 1500, 150, 15, 1.5 and 0.15ppm respectively. The hydrogen peroxide dose of 15ppm equates to an increase in underflow solids content of 14% when compared directly to the control.

The yield stress measurement of the control is 540Pa. Treatment with 15,000ppm hydrogen peroxide reduces the measured yield stress by approximately 86% to 78Pa. 1500, 150, 15, 1.5 and 0.15ppm hydrogen peroxide reduces the yield stress to 76Pa (86% reduction), 65Pa (88% reduction), 116Pa (78% reduction), 117Pa (78% reduction) and 353Pa (35% reduction) respectively.

These results infer that yield stress is not increased by increased solids content when the Polymer D flocculant present in the underflow has undergone treatment via hydrogen peroxide treatment, even at a low dose of 1.5ppm.

Example 9.

Table 8 Influence of Hydrogen Peroxide on settled bed characteristics of Polymer E flocculation for a 4.6%w/v Sand and Gravel washing tailings slurry

Settled Bed Characteristics	Control (0 ppm Hydrogen Peroxide)	Hydrogen Peroxide, ppm				
		15,000	1500	150	15	1.5
Solids, %w/w	35.9	30.0	36.5	37.6	34.5	37.3
Solids, %w/v	46.8	37.1	50.1	51.5	44.4	49.2
Yield Stress, Pa	1187	51	337	877	867	1100

Hydrogen peroxide provides 37.1, 50.1, 51.5, 44,4 and 49.2%w/v solids at 15,000, 1500, 150, 15 and 1.5ppm respectively. At 15,000 and 15ppm this equates to a decrease in underflow solids content of 21 and 5% respectively when compared directly to the control. The solids content achieved at 150ppm equates to an increase 10% when compared directly to the control.

The yield stress measurement of the control is 1187Pa. Treatment with 15,000ppm hydrogen peroxide reduces the measured yield stress by approximately 95.7% to 51Pa although this is at reduced solids content. 1500ppm hydrogen peroxide reduces the yield stress to 337Pa (72% reduction), which is a significant decrease, and at a higher solids content. 150, 15 and 1.5ppm hydrogen peroxide reduces the yield stress to 877Pa (26% reduction), 867Pa (27% reduction) and 1100Pa (7% reduction) respectively.

These results infer that successful increases in compacted solids content in combination with reductions in Yield Stress compared with the Control are achieved with treatment of Polymer E through its combined use with hydrogen peroxide.

Example 10

Influence of oxidising and other reagents on flocculated 4% w/v (2g/l salted) china clay.

In order to test a wide variety of reagents a screening test was devised as follows:-

1. 675 ml of 4% w/v (2g/l salted) china clay was placed in a 1000ml tall form beaker. The contents were stirred at 400rpm using a mechanical gate stirrer. 225 ml of a dilute solution (approximately 0.002% in deionised water) of Polymer E was added and stirring continued for 4 minutes. Stirring speed was reduced to 200rpm for a further 2 minutes. Stirring was then ceased and the time taken for the mudline to settle between the 750ml and the 550 ml marks was recorded. Settlement rate in cm/min was calculated from this figure.
2. The dose of Polymer E required to achieve a settlement rate of around 10cm/min was established from these tests by evaluating a range of solution concentrations. Once this dose had been established the same dose was used for all subsequent tests.
3. The procedure as described under 1 was repeated whereby the dilute solution of Polymer E was prepared in deionised water as a control. Once the initial settlement rate had been measured the sample was left undisturbed for a period of time, it was then stirred at 200rpm for 2 minutes and the settlement time re-measured. This was repeated several times over a period of several hours.
4. To evaluate the different reagents, these were added to the polymer solution prior to addition to the china clay in an amount that resulted in a dose of 1000ppm in the final slurry.

In the results in Table 9 the settlement rate after a total of 18 hours of time had elapsed is quoted. Within this period of time each sample had been stirred and allowed to settle a total of 3 times

Dose of Polymer E used in all tests was 4.0 mg/l. The settlement rate at time zero for the control was 9.8 cm/min.

Table 9

Reagent	Settlement Rate at 18 hours (cm/min)
Control	7.8
Hydrogen Peroxide	0.6
Sodium Perborate	3.8
Sodium Hyperchlorite	0.6
Sodium Persulphate	6.1
Sodium Metabisulphite	4.0
Sodium Bisulphite	3.3
Ammonium Persulphate	1.8
Sodium Nitrite	8.1
Sodium Nitrate	8.1

Reagents that resulted in a significantly lower settlement rate than the control indicate that degradation of the flocculant or floc structure has taken place to a greater degree than through simple mechanical stirring. In the above table all reagents that are know as oxidising agents/ free radical sources showed degradation of the floc to a greater or lesser degree.

Example 11

Table 10 Influence of oxidising reagents on flocculated 4% w/v (adjusted pH 2 using sulphuric acid) china clay.

This substrate is intended to be representative of substrates encountered in hydrometallurgical processes involving acid leaching e.g. copper, electrolytic zinc etc.

The test procedure as described under example 10 was used, but using Polymer B and 4% w/w china clay adjusted to pH 2 as substrate.

In the results below the settlement rate after a total of 21 hours of time had elapsed is quoted. Within this period of time each sample had been stirred and allowed to settle a total of 4 times.

Dose of Polymer B used in all tests was 18 mg/l. The settlement rate at time zero for the control was 9.3 cm/min.

In this series of tests a range of dose levels of the reagents was added as indicated in the table below.

Reagent	Dose (ppm)	Settlement Rate at 21 hours elapsed time
Control	-	9.3
Hydrogen Peroxide	100	0.7
	350	0.6
	600	0.5
	1000	0.5
Sodium Perborate	100	0.6
	350	0.7
	600	0.6
	1000	0.6
Sodium Hypochlorite	100	3.1
	350	6.9
	600	3.1
	1000	3.2

All 3 reagents showed degradation of the flocs over the time period investigated.

Example 12

Table 11 Influence of hydrogen peroxide on flocculated 4% w/v (containing 33.3g/l sodium hydroxide) china clay.

This substrate is intended to be representative of substrates encountered in hydrometallurgical processes involving alkali leaching e.g. alumina, or other alkaline systems.

The test procedure as described under example 11 was used, but using Polymer F and 4% w/w china clay containing 33.3g/l sodium hydroxide as test substrate.

In the results below the settlement rate after a total of 21 hours of time and 66 or had elapsed is quoted. Within this period of time each sample had been stirred and allowed to settle a total of 3 times at 21 hours and 5 x at 66 hours. Dose of Polymer F used in all tests was 3.3 mg/l. The settlement rate at time zero for the control was 9.3 cm/min.

Dose of Hydrogen Peroxide	Settlement Rate at 21 hours elapsed time	Settlement Rate at 66 hours elapsed time
Control	10.2	6.9
100	7.6	8.1
350	11.3	14.6
600	11.2	10.9
1000	8.8	9.4

Under these conditions hydrogen peroxide is ineffective indicating that it will be necessary to have a range of reagents for differing circumstances.

Example 13

Table 12 Influence of Sodium Hypochlorite and Sodium Perborate on flocculated 4% w/v (containing 33.3g/l sodium hydroxide) china clay.

The test procedure as described under example 13 was used, but using Polymer F and 4% w/w china clay containing 33.3g/l sodium hydroxide as test substrate.

In the results below the settlement rate after a total of 26 hours of time and 90 hours of time had elapsed is quoted. Within this period of time each sample had been stirred and allowed to settle a total of 3 times at 26 hours and 4 x at 90 hours.

Dose of Polymer F used in all tests was 3.3 mg/l. The settlement rate at time zero for the control was 9.6 cm/min.

Reagent	Dose of Reagent	Settlement Rate at 21 hours elapsed time	Settlement Rate at 66 hours elapsed time
	Control	10.2	7.7
Sodium Hypochlorite	100	8.9	5.2
	350	9.6	4.4
	600	7.3	No result taken
	1000	4.3	1.5
Sodium Perborate	100	15	5.5
	350	6.3	5.5
	600	12.7	5.3
	1000	11.7	4.2

Both these reagents achieved degradation over a long period of time.

Example 14

Tabel 13 The influence of Hydrogen Peroxide on tailings from a granite quarrying operation

The test procedure as described under example 13 was used, but using Polymer G and tailings from a granite quarrying operations at 3%w/v solids was used as test substrate.

In the results below the settlement rate after a total of 20 hours of time had elapsed is quoted. Within this period of time each sample had been stirred and allowed to settle a total of 6 times.
Dose of Polymer G used in all tests was 1.5 mg/l. The settlement rate at time zero for the control was 8.2 cm/min.

Dose of Hydrogen Peroxide (ppm)	Settlement Rate at 20 hours elapsed time
Control	6.4
1	6.9
5	5.2
10	3.9
100	3.0
500	0.8

These results showed that hydrogen peroxide does cause degradation of the flocs formed in this effluent but at least 5ppm is required to have any effect and the best results are obtained at > 100ppm.

Example 15

Table 14 The influence of Hydrogen Peroxide on settled bed characteristics of Polymer G flocculation of tailings from a granite quarrying operation

The laboratory procedure followed was as described in example 2 with the exception that tailings from a granite quarrying operation at 3% solids was used in place of the china clay slurry and Polymer G was used to flocculate the sample at a dose level of 1.5 mg/l.

Settled Bed Characteristics	Control (0ppm Hydrogen Peroxide)	Hydrogen Peroxide (ppm)		
		10	100	500
Solids Content % (w/w)	46.9	44.3	46.6	47.4
Yield Stress (Pa)	99	10	29	4

These results show that the yield stress in the underflow is significantly lower than that of the control sample at similar solids content. It also confirms that the tests described in example 14 provides a good indication of the reagents that will beneficially affect underflow characteristics.

Example 16

Table 15 The influence of Hydrogen Peroxide on settled bed characteristics of Polymer D, Carboxymethyl cellulose (CMC) and blends of Polymer D and CMC flocculation of 6% w/v (2g/l salted) china clay.

The laboratory procedure was as described in example 2. Due to differing flocculation abilities of CMC and Polymer D, different dose levels of the individual polymers and the blends were required to achieve the appropriate level of flocculation.

Settled Bed Characteristics	Control (0ppm Hydrogen Peroxide)	Hydrogen Peroxide (ppm)			
		15	150	1500	15000
Flocculated using 11.5 mg/l Polymer D					
Solids Content % (w/w)	40.1	42.3	41.7	41.7	40.2
Yield Stress (Pa)	804	219	91	87	66
Flocculated using 50mg/l CMC					

Solids Content % (w/w)	38.7	38.3	37.7	36.5	36.4
Yield Stress (Pa)	718	187	19	11	17
Flocculated using 20 mg/l 80:20 Polymer D :CMC					
Solids Content % (w/w)	38.7	39.0	39.8	39.9	38.6
Yield Stress (Pa)	510	179	163	113	62

These results show that modest increases in underflow solids content are obtained by the addition of hydrogen peroxide when flocculation was achieved using Polymer D and blends of Polymer D and CMC. No increase in underflow solids is observed when flocculation was achieved using CMC alone. However, for all flocculation treatments the addition of hydrogen peroxide provides significant reductions in yield stress, of between 72% and 97%.

Example 17

Table 16 The influence of hydrogen peroxide on 4% (2g/l salted) china clay flocculated with a cationic flocculant -Polymer H. Tests were carried out as described in Example 10, except that Polymer H was used as flocculant, the dose to achieve around 5cm/min was established at 8.8 mg/l, the final settlement rate was measured after 27 hours had elapsed and each sample had been stirred and allowed to settle a total of 8 times in this period.
The settlement rate at time zero for the control was 4.4 cm/min.

Reagent	Settlement Rate at 27 hours (cm/min)
Control	5.8
Hydrogen Peroxide	2.1
Sodium Perborate	<1
Sodium Hyperchlorite	< 1

Example 18

Table 17 The influence of Ozone water on 4% (2g/l salted) china clay flocculated with Polymer D

Tests were carried out as follows. 800 mls of a 4% (2g/l salted) china clay slurry was placed in a 1000ml cylinder. The slurry was stirred meachanically using a paddle stirrer rotating at 900rpm. 20 mls of a 0.05% solution of polymer D was added to the substrate and stirred for 50 seconds. The resultant free settlement rate of the solids mud-line was measured.*1 Once the solids had settled to below the 250 ml mark the contents of the cylinder were stirred for 15 seconds and the free settlement rate again measured. This was repeated as many times as required. When ozone was used, the test was repeated to point *1.Then ozone was bubbled into the sample at a rate of 3l/minute for 15 minutes. The ozone generator was switched off and the whole sample was stirred at 900 rpm for 15 seconds and the settlement rate was re measured.

Test	Comments on Treatment	Settlement Rate hours (cm/min)
Control no flocculant		0.14
Control – 20 mls of 0.05 % polymer D	Initial measurement	13.9
	Re-stirred 1	9.1
	Re-stirred 2	6.9
	Re-stirred 3	5.6
	Re-stirred 4	4.9
	Re-stirred 5	4.4
20 mls 0.05% polymer D	Initial measurement	9.7
	Following ozone treatment	0.41

These results show that the addition of ozone negates the effect of flocculation to such a degree that the settlement rate is close to that of the unflocculated china clay. Mechanical degradation by stirring does not approach this effect.

Example 19

The influence of hydrogen peroxide on the molecular weight of Polymer E in solution.

Procedure

27.82g of 100 volumes (30% w/v) hydrogen peroxide were weighed into a 250ml volumetric flask to produce a 3.338% solution. A double strength, size exclusion chromatography (SEC), mobile phase was also prepared, 11.68g NaCl + 2.28g K_2HPO_4 in a 500ml volumetric flask. An approximately 0.5% solution of Polymer E was prepared in deionised water and tumbled overnight. The dry weight was measured in an oven set at 110C.

A portion of the polymer solution was weighed into a 100ml volumetric flask. 50ml of buffer was added (double strength SEC mobile phase) and the solution was diluted to the mark with the hydrogen peroxide solution. A control sample was prepared in a similar manner but de-ionised water was substituted for the peroxide solution.

One point specific viscosity measurements were made using a Schott 531 10 Ubbelohde capillary viscometer in an AVS 350 automatic viscosity measuring unit.

Polymer E with Hydrogen Peroxide		Polymer E Control
time from start / mins	1 pt sp visc dl/g	1 pt sp visc dl/g
12	23.09	
35		22.78
66	23.02	
129	22.92	
152		22.74
215	22.77	

267		22.65
399	22.43	
412		22.50
1356	21.83	
1385	20.58	
4394		22.32
5786	14.63	

This indicates that hydrogen peroxide does bring about degradation of Polymer E molecular weight.

Claims

1. A process of concentrating an aqueous suspension of solid particles comprising the steps of adding at least one organic polymeric flocculant to the suspension thereby forming flocculated solids in which the flocculated solids are allowed form a layer of solids and thereby forming a more concentrated suspension in which the process comprises the addition of an effective amount of an agent that is selected from the group consisting of free radical agents, oxidising agents, enzymes and radiation,
in which the agent is applied to the suspension prior to or substantially simultaneously with adding the organic polymeric flocculant and/or
the organic polymeric flocculant is added to the suspension in a vessel and the agent is applied to the suspension in the same vessel.

2. A process according to claim 1 in which the agent is selected from perborates, percarbonates, arbonates, persulphates, ozone and peroxides.

3. A process according to claim 1 or claim 2 which the agent is hydrogen peroxide.

4. A process according to any preceding claim in which the agent brings about fragmentation of the flocculated structure.

5. A process according to any preceding claim in which the agent brings about degradation of the organic polymeric flocculant.

6. A process according to any preceding claim in which the agent brings about a reduction in the yield stress of the layer of solids at least 30% below the yield stress of a layer of solids at an equivalent solids content without the addition of the agent.

7. A process according to any preceding claim in which the addition of the agent brings about an increase in the solids content of at least 5% by weight of the layer having a given yield stress compared to a layer having the same yield stress from an equivalent process but in the absence of the agent.

8. A process according to any preceding claim in which the agent evolves a gas.

VT date 15th May 2007

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Patent Department
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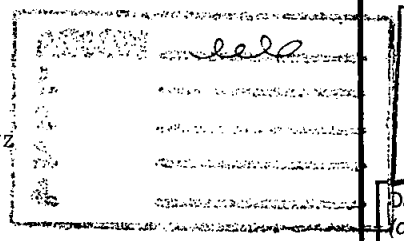
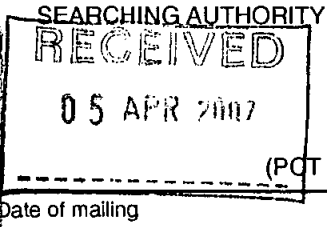
CLECKHEATON ROAD
LOW MOOR
BRADFORD
West Yorkshire BD12 0JZ
GRANDE BRETAGNE





Applicant's or agent's file reference MP/3-22379	Date of mailing *(day/month/year)* 05/04/2007
	FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No. PCT/EP2007/050084	International filing date *(day/month/year)* 04/01/2007

Applicant

CIBA SPECIALTY CHEMICALS HOLDING INC.

1. [X] The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

   Filing of amendments and statement under Article 19:
   The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

   When? The time limit for filing such amendments is normally two months from the date of transmittal of the International Search Report.

   Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Fascimile No.: (41-22) 338.82.70

   For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

   [ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

   [ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

   Shortly after the expiration of **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

   The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

   Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

   In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months.

   See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Isabelle Charles

Form PCT/ISA/220 (October 2005) *(See notes on accompanying sheet)*

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report and the written opinion of the International Searching Authority, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims,description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only (see *PCT Applicant's Guide*, Volume I/A, Annexes B1 and B2).

The attention of the applicant is drawn to the fact that amendments to the claims under Article 19 are not allowed where the International Searching Authority has declared, under Article 17(2), that no international search report would be established (see *PCT Applicant's Guide*, Volume I/A, paragraph 296).

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference MP/3-22379	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/EP2007/050084	International filing date *(day/month/year)* 04/01/2007	(Earliest) Priority Date *(day/month/year)* 18/01/2006
Applicant CIBA SPECIALTY CHEMICALS HOLDING INC.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language**, the international search was carried out on the basis of:
      [X] the international application in the language in which it was filed
      [ ] a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. [ ] **Certain claims were found unsearchable** (See Box No. II)

3. [ ] **Unity of invention is lacking** (see Box No III)

4. With regard to the **title**,
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,
   a. the figure of the **drawings** to be published with the abstract is Figure No. _____
      [ ] as suggested by the applicant
      [ ] as selected by this Authority, because the applicant failed to suggest a figure
      [ ] as selected by this Authority, because this figure better characterizes the invention
   b. [ ] none of the figures is to be published with the abstract

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/050084

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D21/01

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)
B01D

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)
EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/121863 A1 (KELLY JOSEPH M [US] ET AL) 3 July 2003 (2003-07-03) cited in the application abstract; claims; figures paragraphs [0010], [0011]	1-12
A	WO 2004/071989 A (IMERYS PIGMENTS INC [US]; GARSKA MICHAEL J [US]; PRUETT ROBERT J [US];) 26 August 2004 (2004-08-26) cited in the application abstract; claims; figures page 6, paragraph 18 page 24, paragraph 85	1

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document 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 cited 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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 March 2007	05/04/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lapeyrère, Jean

Form PCT/ISA/210 (second sheet) (April 2005)

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/050084

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 685 900 A (YUAN JUN [US] ET AL) 11 November 1997 (1997-11-11) cited in the application abstract; claims column 5, paragraph 9 - paragraph 22	1
A	JP 10 109100 A (TELNITE LTD) 28 April 1998 (1998-04-28) cited in the application abstract	1
A	WO 2005/073132 A (NALCO COMPANY [US]; SARKAR JAWED [US]; BRADEN MICHAEL [US]; SHAH JITEN) 11 August 2005 (2005-08-11) abstract page 6, line 9 - line 20	1

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/050084

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003121863 A1	03-07-2003	NONE	
WO 2004071989 A	26-08-2004	BR PI0406935 A	03-01-2006
US 5685900 A	11-11-1997	AU 703764 B2	01-04-1999
		AU 7027796 A	24-04-1997
		BR 9605152 A	14-07-1998
JP 10109100 A	28-04-1998	NONE	
WO 2005073132 A	11-08-2005	NONE	

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)* see form PCT/ISA/210 (second sheet)	
Applicant's or agent's file reference see form PCT/ISA/220	**FOR FURTHER ACTION** See paragraph 2 below
International application No. PCT/EP2007/050084	International filing date *(day/month/year)* 04.01.2007
Priority date *(day/month/year)* 18.01.2006	
International Patent Classification (IPC) or both national classification and IPC INV. B01D21/01	
Applicant CIBA SPECIALTY CHEMICALS HOLDING INC.	

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	See form PCT/ISA/210	Lapeyrère, Jean Telephone No. +31 70 340-2333

Form (PCT/ISA/237) (Cover Sheet) (April 2005)

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Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

      ☐ a sequence listing

      ☐ table(s) related to the sequence listing

   b. format of material:

      ☐ on paper

      ☐ in electronic form

   c. time of filing/furnishing:

      ☐ contained in the international application as filed.

      ☐ filed together with the international application in electronic form.

      ☐ furnished subsequently to this Authority for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-16
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: US 2003/121863 A1 (KELLY JOSEPH M [US] ET AL) 3 July 2003 (2003-07-03) cited in the application

D1: WO 2004/071989 A (IMERYS PIGMENTS INC [US]; GARSKA MICHAEL J [US]; PRUETT ROBERT J [US];) 26 August 2004 (2004-08-26) cited in the application

D3: US-A-5 685 900 (YUAN JUN [US] ET AL) 11 November 1997 (1997-11-11) cited in the application

D4: JP 10 109100 A (TELNITE LTD) 28 April 1998 (1998-04-28) cited in the application

D5: WO 2005/073132 A (NALCO COMPANY [US]; SARKAR JAWED [US]; BRADEN MICHAEL [US]; SHAH JITEN) 11 August 2005 (2005-08-11)

INDEPENDENT CLAIM 1

1. The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 1 is not new in the sense of Article 33(2) PCT.

   Document D1 discloses (the references in parentheses applying to this document):

   a process of concentrating an aqueous suspension of solid particles comprising the steps of adding at least one organic polymeric flocculant to the suspension thereby forming flocculated solids in which the flocculated solids are allowed form a layer of solids and thereby forming a more concentrated suspension in which the process comprises the addition of an effective amount of oxidising agents, in which the agent is applied to the suspension simultaneously with adding the organic polymeric flocculant and the organic polymeric flocculant is added to the suspension in a vessel and the agent is applied to the suspension in the same vessel. (see paragraphs 10 und 11)

2. Dependent claims 2 to 16 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, the reasons being that the dependent claims are dislosed

in documents D1 to D5. It is currently impossible to distinguish the contribution of the application to the state of the art.

Re Item VIII
Certain observations on the international application

3. The application does not meet the requirements of Article 6 PCT, because claim 1 is not clear.

4. The feature "an effective amount" used in claim 1 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear, Article 6 PCT.
5. The feature "substantially" used in claim 1 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear, Article 6 PCT.

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 10109100
PUBLICATION DATE : 28-04-98

APPLICATION DATE : 04-10-96
APPLICATION NUMBER : 08264344

APPLICANT : TERUNAITO:KK;

INVENTOR : NISHIMURA HIROYUKI;

INT.CL. : C02F 11/14 B01D 21/01 B01F 17/52 C02F 11/06 C02F 11/08

TITLE : VOLUME REDUCTION TREATMENT OF HIGH WATER CONTAINING DREADING BOTTOM MUD

ABSTRACT : PROBLEM TO BE SOLVED: To provide the volume reduction treatment method of high water containing dredging bottom mud suitable to a massive treatment, capable of flocculating the dredging bottom mud without adversely affecting environment and also capable of using a general low pressure dehydrator.

SOLUTION: Sodium polyacrylate 3,000,000 to 5,000,000 in weight average molecular weight and 25-75% in neutralization degree is added to the high water containing dredging bottom mud having a 400-3000% water content ratio to make the dispersion stable, and next a divalent or a trivalent metallic salt aqueous solution is added to form hydrophobic flocks and then the flocks are dehydrated naturally or forcedly, thus the volume of the high water containing dredging bottom mud is reduced.

ISR

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 August 2004 (26.08.2004)

PCT

(10) International Publication Number
WO 2004/071989 A1

(51) International Patent Classification[7]: C04B 33/04, 33/10, B01D 21/01

(21) International Application Number: PCT/US2004/002011

(22) International Filing Date: 9 February 2004 (09.02.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/445,857 10 February 2003 (10.02.2003) US
60/493,809 11 August 2003 (11.08.2003) US

(71) Applicant *(for all designated States except US)*: **IMERYS PIGMENTS, INC.** [US/US]; Suite 300, 100 Mansell Court East, Roswell, GA 30076 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **GARSKA, Michael, J.** [US/US]; 271 South Anderson Drive, Sandersville, GA 31082 (US). **PRUETT, Robert, J.** [US/US]; 113 Cambridge Drive North, Milledgeville, GA 31061 (US). **YUAN, Jun** [US/US]; 119 Springfield Lane, Warner Robins, GA 31088 (US). **GOLLEY, Christopher, R., L.** [GB/US]; 617 Linton Road, Sandersville, GA 31082 (US).

(74) Agent: **GARRET, Arthur, S.**; Finnegan, Henderson, Farabow, Garrett & Dunner, L., L.P., 1300 I Street, Northwest, Washington, DC 20005-3315 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/071989 A1

(54) Title: A METHOD OF TREATING AN AQUEOUS SUSPENSION OF KAOLIN

(57) Abstract: A method for the treatment of kaolin particulate material comprising: providing a dispersed aqueous suspension comprising kaolin particulate material and having a pH of at least about 7.5; selecting at least one selective flocculation polymer, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 1% to about 12%, such as from about 4.5% to about 8%; selectively flocculating said suspension into a first layer and a second layer by adding to said suspension said at least one selective flocculation polymer; and separating said first layer from said second layer.

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A METHOD OF TREATING AN AQUEOUS SUSPENSION OF KAOLIN

[001] This application claims priority to U.S. Provisional Patent Application No. 60/445,857, filed February 10, 2003 and U.S. Provisional Patent Application No. 60/493,809, filed August 11, 2003.

[002] The present invention relates to a method of treating an aqueous suspension of kaolin particulate material with at least one selective flocculation polymer. An advantage of the inventive method may be the ability to separate impurities from the aqueous suspension, which may improve at least one property of the kaolin, including its whiteness, brightness, as well as other properties of the kaolin. The present invention also relates to the selection of selective flocculation polymers with a narrow range of measured anionicity. Advantages associated with selecting such a polymer may include, for example, improved productivity resulting from reduced settling times and reduced dosage of polymer, improved product variability resulting from more reproducible, consistent flocculation over time, and improved reduction in impurities, which may improve at least one of whiteness, brightness, and other properties of the kaolin.

[003] Kaolin, or kaolinitic clay, is a mineral clay containing the particulate mineral kaolinite as its principal constituent. Such clays were formed in geological times by the weathering of the feldspar component of granite. Primary kaolin clays are those which are found in deposits at the site at which they were formed, and are generally present in a matrix of undecomposed granite, which must be separated from the clay during the refining process for the clay. For example, kaolin clays mainly of the primary type are obtained from deposits in South West England, France, Germany, Spain, and the Czech Republic. Secondary kaolin clays, which are alternatively known as sedimentary kaolin clays, are those which were flushed out in geological times from the granite matrix in which they were formed, and were deposited in an area remote from their site of formation, generally in a basin formed in the surrounding strata. For example, kaolin clays obtained

from deposits in Georgia, South Carolina, and Alabama, USA are generally of the sedimentary (secondary) type.

[004] Kaolin clay is refined and used as an ingredient, a pigment, and a filler material in a variety of application compositions, especially for filling and coating of paper, paper board, and like products. Kaolin is a white mineral and is often used in such application compositions to impart, among other properties, whiteness and brightness. However, one or more desirable properties of the kaolin may be adversely affected by the presence of impurities. Kaolin clays are generally found in association with impurities, which are often present in relatively small proportions. The composition and nature of the impurities can vary considerably, depending on the geographical region from which the kaolin clay is obtained. The impurities present can significantly affect various properties of the kaolin clay.

[005] The present invention also relates to the treatment of kaolin clays containing separable impurities therein with a selective flocculation polymer, such as a selective flocculation polymer with a narrow range of measured anionicity, in order to reduce the amount of such impurities present in the kaolin clays. The present invention further relates to the treatment of kaolin clays containing separable impurities therein with a selective flocculation polymer manufactured in a continuous process and having a narrow range of measured anionicity, to reduce the amount of such impurities that are present.

[006] Particular impurities, which when present in kaolin are often desirable to remove, include titanium compounds present as, for example, titania. This impurity is colored and its presence adversely affects the whiteness and brightness of the kaolin. The titania often contains at least a small percentage of associated iron oxide, which either stains the surface of the titania crystals or acts as a substituent in the titania lattice. It is the colored iron oxide associated with, but not easily separable from, the titania, which principally causes the unwanted whiteness and brightness reduction.

Titania impurities are found mainly in sedimentary kaolins, for example from the southeastern United States, and it is often desirable to remove such impurities from such kaolins.

[007] Other impurities, for example, quartz, mica, phosphates, fine clay impurities such as certain smectite clay constituents, and various other species, e.g., compounds containing transition elements such as iron, may also be present, and may be undesirable in many kaolin product applications. In general, such impurities may be found in either primary or sedimentary kaolin clays. However, the nature and amount of the impurity types present will vary between clay types.

[008] Improving the properties of kaolin clays, especially the whiteness and brightness of kaolin clays, by the separation therefrom of separable impurities such as titania and iron oxides, has been a problem facing the kaolin industry. While selective flocculation has proven to be a possible solution to this problem, variability in the flocculation process has been found to create undesirable variability in many kaolin product applications. Many attempts have been made to solve this problem but none has been entirely satisfactory.

[009] When particles of mineral ore or powder mixtures are sufficiently large, for example, larger than 325 (U.S.) mesh, the components of the mixture can be separated by simple physical means such as air or magnetic separation. When particles are finer, more sophisticated technology may be needed to bring about efficient separations. It is conventional to make the separation of finely divided mineral, *e.g.*, particles finer than 325 mesh, by forming the mixture into an aqueous suspension or slurry and providing physical and/or chemical treatments that will bring about a desired separation.

[010] Certain physical beneficiation processes such as magnetic separation (*e.g.*, as described in WO 98/50161A) and particle size classification, *e.g.*, by centrifuging (*e.g.*, as described in U.S. Patent No. 4,018,673), have been applied. Likewise, certain chemical beneficiation

methods have been proposed for employment to separate fine impurities, especially discoloring titania impurities, from kaolin clays to improve their properties, such as their brightness. For example, for this purpose flotation has been described in U.S. Patent No. 3,655,038, froth flotation has been described in U.S. Patent No. 4,472,271 and EP 0 591 406, and leaching has been described in U.S. Patent No. 4,650,521. Substantial industrial use has been made of froth flotation; however, this process is expensive to operate.

[011] Selective flocculation is a procedure that is widely used commercially to separate finely divided minerals and powders. In the case of clay, some processes utilize anionic polymers to selectively flocculate the clay, leaving the impurities, such as titanium, in the form of titania, dispersed and amenable to subsequent separation from the clay. Commercial variants of selective flocculation employ weakly anionic polymers such as hydrolyzed polyacrylamide to selectively flocculate impurities in the precipitate, leaving the purified clay dispersed in the supernatant. *See, for example*, U.S. Patent Nos. 3,371,988, 3,701,417, 3,837,482, 3,862,027, 4,227,920, 4,604,369, 5,535,890, 5,685,900, and WO 98/5788.

[012] In U.S. Patent No. 3,701,417 and WO 98/57888, the process described is of a kind operated under conditions such that the titania and other impurities are separated in a flocculated layer and the product is recovered from a deflocculated layer. In other instances, the titania and other impurities are separated in a deflocculated layer. Separating the impurities in a flocculated lower layer, or so called underflow layer, is not fundamentally an efficient process because a significant amount of kaolinite, *e.g.*, 20% or more, typically 30% to 45% by weight, of the feed material becomes entrained with the impurity, *e.g.*, titania. Separating the impurity in a deflocculated layer is much more efficient, *e.g.*, the amount of kaolinite present in the impurity layer can be small, *e.g.*, at most a few per cent by weight. The present invention also relates to use of selective flocculation of the latter type, wherein the

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separable impurities such as titania are separated in a deflocculated upper, or so-called overflow, layer.

[013] The methods of the latter type, *i.e.*, which involve separating impurities in a deflocculated layer, as described in the aforementioned prior patents, are not effective and versatile, for example, as compared with the method of the present invention, at least because they rely on the use of a particular feed kaolin and/or on the use of one or more preceding beneficiation steps. For example, the method of U.S. Patent No. 5,685,900 requires the feed clay itself to be fine and bright and to have been pre-treated by particle size classification and oxidative bleaching prior to selective flocculation. The method of U.S. Patent No. 4,227,920 relies on prior treatment of the feed kaolin by high gradient magnetic separation and grinding. The method of the invention beneficially is not limited by the source of the feed clay or the need for preceding beneficiation steps.

[014] One theory for the success of selective flocculation is that the polymer is selectively absorbed. To achieve selective adsorption of a flocculating agent on a particular component of a mixture, a number of methods have been suggested in the literature [Yu and Attia; in "Flocculation in Biotechnology and Separation Systems," (Y. A. Attia, ed.) p. 601, Elsevier, Amsterdam 1987; Behl, S. and Moudgil, B. M., Minerals and Metallurgical Processing, 5, 92,1992 and, Behl, S. and Moudgil, B. M., Journal of Colloidal Interface Science, 160, 1993]. Because clay particles are naturally charged on their surfaces, it is much easier and more effective to flocculate the clay particles rather than the impurities.

[015] One aspect of the present invention is a method of treating an aqueous suspension of kaolin particulate material, whereby impurity particles are separated from the kaolinite in the material by selective flocculation of the kaolinite and deflocculation of impurity particles. This method comprises the selection of a selective flocculation polymer with a narrow range of measured anionicity. Desirably, the treatment allows such separation to be carried out

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efficiently, more effectively, and/or in a more versatile manner than prior art treatments.

[016] This and other objects may be met by the method of the invention and any benefits thereby obtained will become apparent from the description later in this specification.

[017] According to one aspect of the present invention, there is provided a method for the treatment of kaolin particulate material comprising:

(a) providing a dispersed aqueous suspension comprising kaolin particulate material and having a pH of at least 7.5;

(b) selecting at least one selective flocculation polymer, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 1% to about 12%.

(c) selectively flocculating said suspension into a first layer and a second layer by adding to said suspension said at least one selective flocculation polymer; and

(d) separating said first layer from said second layer.

[018] According to a second aspect of the present invention, there is provided a method for the treatment of kaolin particulate material comprising:

(a) providing a dispersed aqueous suspension comprising kaolin particulate material and having a pH of at least 7.5;

(b) selecting at least one selective flocculation polymer, wherein said at least one selective flocculation polymer has a narrow range of variability for measured anionicity and has a measured anionicity ranging from about 1% to about 12%;

(c) selectively flocculating said suspension into a first layer and a second layer by adding to said suspension said at least one selective flocculation polymer; and

(d) separating said first layer from said second layer.

[019] According to a third aspect of the present invention, there is provided a method for the treatment of kaolin particulate material comprising:

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(a) providing a dispersed aqueous suspension comprising kaolin particulate material and having a pH of at least 7.5;

(b) selecting at least one selective flocculation polymer, wherein said at least one selective flocculation polymer has been manufactured by a continuous process and has a measured anionicity franging from about 1% to about 12%;

(c) selectively flocculating said suspension into a first layer and a second layer by adding to said suspension said at least one selective flocculation polymer; and

(d) separating said first layer from said second layer.

[020] The kaolin particulate material treated by the method of the invention may contain at least 0.1% by weight, in many cases at least 1.0% by weight, and in some cases at least 1.5% by weight, of at least one impurity such as, for example, titania and/or mica, based on the dry weight of the kaolin. The titania, if present, may comprise the anatase and/or rutile form of TiO_2.

[021] Other undesirable impurities, especially fine impurities, associated with kaolin, such as one or more of feldspar, silicates such as quartz, clay mineral impurities such as smectites and other kandites, phosphates and metal oxides, e.g., of iron and other transition metals, may, alternatively or in addition to titania and mica, be separated by the method of the invention either used alone or in conjunction with one or more other known beneficiation processes.

[022] The dispersed aqueous suspension may be formed by mixing dry kaolin particulate material with water. Alternatively, the suspension may be formed by taking an existing suspension of kaolin particulate material and adding water as needed. In either case, a dispersant may be needed. When blunged, an aqueous suspension may have a solids content of at least 35%, for example, ranging from about 40% to about 70% or more by weight. When flocculated, an aqueous suspension may have a solids content of less than

35%, for example, ranging from about 5% to about 20% by weight or from about 10% to about 15%.

[023] The pH in steps (a) and (c) is desirably at least about 7.5, for example, at least about 9.5, or at least about 10.2. In one embodiment, the pH ranges from about 10.5 to about 12.5, such as about 11.5. According to one aspect of the invention, the adjustment of pH to a value of at least about 9.5 is carried out suitably before addition of the polymer in step (c).

[024] Where selective flocculation has been applied industrially in the prior art to remove impurities from kaolin, the pH has generally been not greater than 9.5. The benefit of using, in conjunction with conditioning, a higher pH for selective flocculation of kaolinite especially aimed at separation and removal in a deflocculated form of fine titania has not previously been recognized.

[025] Use of a selective flocculation process to treat kaolin at a higher pH is known from U.S. Patent No. 3,539,003 and subsequent GB-A-2059811B. However, the treatments described in those documents are directed at treating kaolin clays from England which do not contain separable titania. Furthermore, in the method of U.S. Patent No. 3,539,003, it was considered essential to add an additive such as a calcium salt to provide multivalent ions. No such additive is required in the method of the invention.

[026] At least 95%, in many cases at least 97%, by weight of the kaolinite present in the aqueous suspension in step (a) may be separated and recovered from the flocculated product layer in step (d) in the method of the invention. At least 20% by weight, e.g., at least 30% to at least 40% by weight or more, for example, at least 50% by weight, of the impurities present in the aqueous suspension in step (a) may be separated from the deflocculated product layer in step (d) by the method of the invention. Further TiO_2 content and other impurities may be separated by one or more other conventional beneficiation processes, which may be applied, for example, after the selective flocculation separation process.

[027] "Dispersed aqueous suspension" refers to an aqueous suspension, wherein insoluble and possibly soluble components are uniformly dispersed in a medium, such as water. Dispersal of the insoluble and possibly soluble components may be facilitated by one or more pH modifiers, dispersants, deflocculants, etc.

[028] "Selective flocculation" refers to the combination or aggregation of a select subset of insoluble particles caused by the addition of at least one suitable flocculation polymer to a suspension of a kaolin particulate material. By increasing the effective particle size of the insoluble components present in the suspension, the efficiency of solid/liquid separation techniques (*i.e.*, separation of impurities) is improved.

[029] "Measured anionicy" (or measured charge density) refers to the total charge density, which includes charge resulting from the copolymerization reaction (i.e., theoretical charge density), plus the charge contribution originating from hydrolysis of functional groups.

[030] "Narrow range of variability" refers to a narrow range of variability in a measured property on a batch-to-batch basis. The range of variability is deemed to be narrow when the measured property over fifteen batches has a 3 sigma of +/- 10% of the measured mean.

[031] "Separation" refers to the removal of the supernatant, which primarily contains the impurities, from the precipitate, which primarily contains the kaolin particles, following selective flocculation.

[032] It has been found, surprisingly and beneficially, that the method of the present invention, wherein the selective flocculation polymer is specifically selected such that it has a measured anionicity ranging from about 1% to about 12% may improve the productivity by providing reduced settling times and allowing for reduced dosage of polymer. In one embodiment, the selective flocculation polymer is selected such that has a measured anionicity ranging from about 4.5% to about 8%, such as from about 6% to about 7%. The present invention may also allow for reduced product variability by

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providing a more reproducible process, and may also allow for a reduction in impurities, which may improve at least one of whiteness, brightness, and other properties of the kaolin. It has been found, surprisingly and beneficially, that the method of the present invention, wherein the selective flocculation polymer is selected from polymers with a narrow range of variability for measured anionicity, such as those manufactured by a continuous process, may improve productivity and reduce product variability.

[033] Another benefit of the method of the present invention is that it allows titania-containing impurities and other fine, undesirable impurities in kaolin to be reduced to levels such that other conventional kaolin treatment processes, which may also beneficially be used in treatment of the kaolin, may be applied more effectively. For example, such other processes, which may be applied after selective flocculation, may comprise one or more of oxidation; particle size classification; comminution, *e.g.,* by grinding using particulate grinding media; magnetic separation; bleaching; and dewatering.

[034] A further benefit of the method of the invention is that it may be applied as at least one of various stages of a multi-stage kaolin beneficiation route. For example, it is possible to apply the method of the invention before other beneficiation stages, such as before one or more of oxidation, comminution (for example, grinding), particle size classification (for example, centrifugation), magnetic separation, and bleaching. Thus, the kaolin particulate material employed in the method of the invention may comprise crude kaolin which, apart from an optional degritting step applied before or during the method, need not be subject to any other particle separation or beneficiation steps until after treatment by the method of the invention.

[035] A still further benefit is that the fineness and brightness of the feed kaolin treated by the method of the invention are not critical for the method to be effective, as distinct from prior art methods, *e.g.,* as described in U.S. Patent No. 5,685,900. For example, the kaolin treated by the method of the invention may comprise a coarse crude kaolin clay having a (water

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washed) GE brightness of less than 70, *e.g.*, in the range of from 20 to 70, although kaolin having a GE brightness of greater than 70 may also be treated by the method. All brightness values referred to herein are as measured according to the standard TAPPI procedure T-646 05-75.

[036] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate one possible embodiment of the invention and together with the description, serve to explain, but not limit, the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[037] Figure 1 is a diagrammatic flow sheet of a method of treating an aqueous kaolin suspension in accordance with an embodiment of the invention.

[038] Figure 2 is a graph comparing remaining titania after selective flocculation versus % anionicity of the selective flocculation polymer.

[039] Figure 3 is a graph comparing needed dosage of selective flocculation polymer versus % anionicity of the selective flocculation polymer.

[040] Figure 4 is a graph comparing settling times after selective flocculation versus % anionicity of the selective flocculation polymer.

[041] The method of the invention may be operated as a batch, semi-continuous, or continuous process.

[042] The kaolin particulate material for treatment according to the method of the present invention may be selected from primary and secondary kaolin clays. In one embodiment, the kaolin particulate material is selected from secondary kaolin clays, for example, those obtained from one of the deposits in Georgia, USA. The starting material may comprise a substantially dry, kaolin particulate material, further comprising at least one impurity, for example, those chosen from titania and mica.

[043] This starting material may be treated by adding water and at least one optional dispersant (dispersing agent) thereto to produce the dispersed aqueous suspension of step (a). In one embodiment, mechanical

working, e.g., by blunging, can be applied to the aqueous suspension produced in step (a), whereby agglomerates present in the kaolin are broken down by the working process. The mechanical working is desirably carried out before any conditioning step and may be applied during step (a). Addition of dispersant and/or application of working may be applied in a batch, semi-continuous, or continuous process.

[044] Non-limiting examples of suitable dispersants that may be included in the aqueous suspension of kaolin particulate material of step (a) include anionic dispersants, known to be useful in a deflocculation/selective flocculation separation process. For example, the dispersant may comprise an inorganic agent, such as an alkali metal silicate, *e.g.,* sodium silicate or potassium silicate, or a condensed phosphate salt, such as sodium hexametaphosphate or sodium pyrophosphate. Alternatively, or in addition, the dispersant may comprise an organic agent such as a lignosulfonate, *e.g.,* sodium lignosulfonate, or a polycarboxylate, *e.g.,* a polyacrylate, such as a sodium polyacrylate.

[045] If the dispersed aqueous suspension is treated by the mechanical working process, the particle solids concentration may be at least about 35%, for example, the concentration may range from about 40% to about 70% or more by weight. According to another aspect, the solids concentration in the suspension is at least about 50%, at least about 60%, or even about 70% or more by weight. A work input of at least 5kJ/kg, for example, at least 15kJ/kg, *e.g.,* from 20kJ/kg to 100kJ/kg, may be applied during the mechanical working process.

[046] Following step (a), including any mechanical working applied, the suspension may optionally be diluted and degritted to remove large particles still present therein.

[047] The pH may be adjusted more than once prior to step (b). For example, the pH may be adjusted to be at least about 7.5, such as at least about 9.5, or to range from about 10.5 to about 12.5. In one embodiment, the

pH is adjusted to about 11.5. Any pH adjustment may each be carried out by adding one or more suitable basic substances, for example, those chosen from alkali metal hydroxides and carbonates and ammonium hydroxides and carbonates, such as sodium hydroxide, potassium hydroxide, sodium carbonate and ammonium hydroxide. In one embodiment, sodium hydroxide is used as the pH adjusting additive.

[048] It has been found that if the polymer is added soon after step (a), with the pH not being at least about 7.5, the resulting flocs are relatively fine and take a long time to settle. This is undesirable at least because it reduces product throughput. Furthermore, it has been found that this can increase the amount of impurity present in the underflow or product layer in the separation by selective flocculation.

[049] An optional conditioning step may be applied before a pH adjustment, which would be prior to the addition to the suspension of the selective flocculation polymer in step (c). The optional condition step may improve the size and strength of the flocs, which are produced after the selective flocculation polymer has been added, and thereby improve the effectiveness and efficiency of the separation process, i.e., separation of kaolinite flocs from deflocculated impurities.

[050] When applied, conditioning by ageing is carried out for a period of at least about 30 minutes, usually at least about 2 hours. Ageing for a period of at least about 5 hours, for example, for a period of at least about 8 to about 24 hours, or for a period of about 1 to about 7 days, prior to selective flocculation polymer addition, may be beneficial.

[051] Where the optional conditioning step includes, in addition to or instead of ageing, the addition of at least one conditioning chemical, the at least one conditioning chemical is desirably added prior to ageing. One or more conditioning chemicals may, however, be added after some or all of the ageing. The conditioning chemicals may, for example, comprise one or more salts of a monovalent ion metal, for example one or more sodium salts. The

sodium salt(s) may comprise an organic salt such as a salt of a polycarboxylate, or a halide, such as sodium chloride and/or sodium polyacrylate. Sodium polyacrylate may be employed as a mineral dispersant. In one embodiment, sodium chloride solution, having a concentration ranging from about 10% to about 25% by weight, is added to the clay slurry in an amount ranging from about 5 to about 40 pounds, for example, about 20 pounds per dry ton of kaolin particulate material.

[052] The optional conditioning chemical(s) may be added to the kaolin suspension via one or more static in-line mixers. Alternatively, the chemical(s) can be added to the kaolin suspension in one or more conventional mixers using mechanical agitation means to ensure good mixing.

[053] The optional conditioning step may be preceded by a pH adjustment step, after or during step (a). According to one aspect, the pH may be adjusted to at least about 6.5; for example, the pH may be adjusted to range from about 6.5 to about 9.5. According to another aspect, the pH may be adjusted to range from about 6.5 to about 7.5 at some time prior to the optional conditioning step.

[054] The at least one selective flocculation polymer added in step (c) is suitably mixed with the kaolin suspension prior to delivery of the mixture of the two to the selective flocculation separator. Conveniently, these two ingredients are thoroughly mixed together prior to delivery to the separator. The at least one selective flocculation polymer may be added via one or more static in-line mixers. Alternatively, the at least one selective flocculation polymer can be added to the kaolin suspension in one or more conventional mixers using conventional mechanical agitation means to ensure good mixing. The at least one selective flocculation polymer may be added in one or more doses at one or more addition points prior to delivery of the suspension to the separator.

[055] The feed aqueous suspension to be delivered to the selective flocculation separator may have a specific gravity in the range of from about

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1.03 to about 1.15. The solids content of the suspension may accordingly be less than about 35%, such as in the range of about 5% to about 21%, e.g., about 10% to about 15%, by weight. Dilution with water may be carried out before the delivery to the separator, for example, before addition of the selective flocculation polymer.

[056] The feed aqueous suspension to be delivered to the selective flocculation separator, e.g., after any optional conditioning and prior to selective flocculation polymer addition, may beneficially be heated. For example, the suspension may be heated by use of hot water in a water dilution stage and/or by passage of the suspension through an external heater, e.g., a heating jacket of a heat exchanger, e.g., to raise the temperature by at least about 10°C. In one embodiment, the suspension is heated from about 15-20°C to about 30-35°C or more.

[057] The at least one selective flocculation polymer selected in step (b) and added to the suspension in step (c) of the method of the invention is chosen on the basis of the polymer's measured anionicity. U.S. Patent Nos. 4,798,653 and 6,307,013 have reported standard flocculation polymers having a measured anionicity ranging from about 1% to about 40%. However, it has been discovered that distinct process and product advantages are possible where the measured anionicity ranges from about 1% to about 12%, for example, from about 4.5% to about 8% or from about 6% to about 7%, as reported in Figures 2-4.

[058] Assessment of the anionicity (*i.e.*, charge density) of a polymer can be reported in two ways. The first and more common practice is to report the molar percentage of the monomer (which contains the anionic charge group) in the monomer reaction feed. This percentage is referred to as the "theoretical" anionicity or "theoretical" charge density. For example, an acrylamide/acrylate copolymer derived from a mixture of monomers, wherein 10% of the monomers are acrylate monomers, has a theoretical anionicity of 10%.

[059] The other method of reporting anionicity is based on a titration method that measures the "total" charge density of the test polymer. This method includes not only the charge density contributions from the monomers, but also includes the anionicity that results from hydrolysis of various groups that occurs during a polymerization reaction. For example, a hydrolysis reaction can convert a significant number of amide groups to carboxyl groups, as much as 7% for low charge density polymers (as in the case of the Floerger AN 905 PWG polymer). Without being bound by any particular theory or mechanism, it is believed that it is the total, or measured, anionicity that dictates how well a given polymer performs in the method of the invention.

[060] A selective flocculant used in this invention can have any molecular weight that does not adversely effect the desired flocculation of the kaolin particles and deflocculation of the impurities. Higher molecular weights may provide improved flocculation performance. Typically, the average molecular weight will range from about 100,000 to about 50,000,000 or more. According to one aspect, the molecular weight is greater than about 100,000, for example, greater than about 1,000,000, and greater than about 10,000,000, provided the molecular weight does not adversely effect the desired flocculation reaction.

[061] The organic polymers useful as the selective flocculation polymer in carrying out the method of the invention include, by way of example, water-soluble weakly anionic organic polyelectrolytes. Weakly anionic polymers may contain both anionic and non-ionic groups. Anionic properties may be imparted to synthetic non-ionic organic polymers, for example by the presence of side chains of anionic groups, such as carboxylic acid, carboxylic anhydride and carboxylic acid salt groups. Non-ionic groups in a side chain in the polymer may also be present, resulting from the presence of certain hydrophilic groups, *e.g.*, one or more of the following

hydrophilic groups: carboxylic acid amide, carboxy alkyl ester, pyrrolidone, hydroxy, hydroxy alkyl ether and alkoxy.

[062] The anionic features of the polymeric flocculants can be imparted by any appropriate chemical constituents present on the polymer. Anionic polymers containing carboxyl, carboxymethyl, phosphate and sulfate functionalities, for example, are suitable for the invention. Non-limiting examples of suitable flocculants according to this invention include anionic polyacrylamides and anionic polysaccharides.

[063] Because of their commercial availability, high molecular weight weakly anionic synthetic polymers, such as polyacrylamides containing some replacement, for example from 1% to 4% by weight of amide groups by carboxylic groups, are also suitable for the purposes of the invention. Such polyelectrolytes are prepared by copolymerization of the non-ionic monomer(s), *e.g.*, acrylamide, and one or more suitable carboxylic acids, *e.g.*, acrylic acid, or by the partial hydrolysis of non-ionic polymer(s), *e.g.*, polyacrylamide. Polyacrylamides with carboxyl groups represent one preferred class of flocculants for use in this invention. In one embodiment, the at least one selective flocculation polymer is selected from acrylamide/acrylic acid copolymers, such as ULTIMER 00LT053 from ONDEO Nalco Co.

[064] The at least one selective flocculation polymer may be added to the suspension in the form of a powder, a suspension, or a solution. The concentration of the polymer in the suspension, after being added to the suspension in step (c) of the method of the invention, may range from about 0.01% to about 0.5%, such as from about 0.05% to about 0.5% by weight based on the dry weight of kaolin present. When provided as a solution or suspension, the at least one selective flocculation polymer may be diluted in the solution/suspension to a concentration ranging from about 0.025% to about 0.25%, such as from about 0.05% to about 0.1% by weight, based on the total weight of the solution. In one embodiment, the at least one selective flocculation polymer is added to the suspension in the form of a solution,

wherein the polymer is present at a concentration of about 0.075% by weight, based on the total weight of the solution.

[065] The at least one selective flocculation polymer selected in step (b) and added to the suspension in step (c) of the method of the invention may be chosen on the additional basis that the at least one selective flocculation polymer has a narrow range of variability for measured anionicity. Heretofore, batch to batch variability in the measured anionicity of the polymer has not been a concern of manufacturers and consumers of flocculation polymers. Yet the present inventors have discovered that variability, presumably in the manufacturing process, results in variability in measured anionicity and, consequently, variability in selective flocculation and final kaolin product quality and yield. It has been discovered that certain selective flocculation polymers have a narrow range of variability for measured anionicity, particularly selective flocculation polymers manufactured by continuous processes.

[066] In the selective flocculation processes of step (c), when the at least one selective flocculation polymer is added to the suspension, a flocculated phase containing kaolin particles forms and settles as a dense, viscous, gelatinous bottom layer; the top layer is a dispersed fluid suspension containing the deflocculated impurities. In the instance where a kaolin clay is selectively flocculated in this manner, the bottom layer contains a high percentage of the kaolin particles present and some impurities, and the top layer contains a high percentage of impurities and a small amount of kaolin particles.

[067] The specific gravity of the supernatant or deflocculated impurity-containing aqueous layer produced by separation from kaolinite in the selective flocculation process in step (c) of the method according to the invention may be about 1.001 or more, e.g., in the range about 1.001 to about 1.03. Adjustment of the specific gravity may be made by adjustment of the dose of the at least one selective flocculation polymer added to the

suspension to be treated. In one embodiment, the process of measuring specific gravity of the supernatant with a hydrometer, adding additional polymer while mixing, and allowing the flocs to settle is repeated until the specific gravity is less than about 1.004. A specific gravity of about 1.004 or less may ensure high recovery of the precipitate or flocculated clay, while minimizing the loss of fines in the supernatant.

[068] Following formation of the layers in step (c), the layer of deflocculated impurities may be separated from the layer of flocculated kaolin particles in step (d) by conventional means, *e.g.*, elutriation, decanting or siphoning using batch operation or in a continuous separator. The flocculated kaolin suspension extracted in step (d) may be further treated in a known manner, for example, by optional high shear pumping or mixing to break up the flocs, followed by one or more further beneficiation processes, *e.g.*, one or more of oxidation, comminution (*e.g.*, grinding), particle size classification (*e.g.*, screening and/or centrifugation), magnetic separation, bleaching, washing, and dewatering (*e.g.*, spray drying). Treatment with an oxidizing agent may oxidize residual polymers and other oxidizable impurities present in the suspension following the selective flocculation process.

[069] After separation of the flocculated kaolin product suspension and before further processing of the same, the pH of the flocculated kaolin product suspension may be reduced in a well-known way by adding an acidic substance, for example to a pH of about 7 or less.

[070] Prior to or during further processing, the flocculated kaolin suspension extracted in step (d) may be further treated in at least one additional selective flocculation step in order to provide even further purification of the kaolin. For example, the suspension obtained may be cleaned by washing with clean water, and treated by repeating one or more of the steps previously applied prior to selective flocculation polymer addition. Further selective flocculation polymer, which may be the same as or different from that selected in the earlier step (b) and employed in the earlier step (c),

may then be added at the appropriate stage. The suspension is again allowed to separate in a selective flocculation separator, and the respective layers formed are subsequently extracted as in the earlier selective flocculation and extraction steps.

[071] The separated and extracted impurity-containing deflocculated material may be discarded or further treated to recover, purify, and use ingredients therein, such as TiO_2. Water in the material may be separated by dewatering and may be purified and recycled for re-use in the same process or in a different process in a known manner.

[072] As described earlier, the resulting kaolin, optionally after at least one additional further processing step, may show at least one property superior to those obtained by prior art processes. The resulting kaolin may, for example, have the following product properties:

% residual TiO_2: <0.7% by weight (based on the dry weight of kaolin);

GE brightness: at least 88, such as at least 91.

[073] Although the invention is effective in treating kaolin-containing inorganic particulate materials having a wide range of particle size properties, it is also suitable for producing fine materials suitable for use as pigments in paper products. For example, the product produced may have the following properties:

mean particle size: from about 0.2 μm to about 5 μm, *e.g.*, from about 0.2 μm to about 1.5 μm;

percentage (by weight) of particles having a size less than 2 μm: at least 60%, in some cases at least 80%, for very fine clays at least 90% by weight.

[074] In this specification, titania and iron oxide amounts are as measured by a Philip Minimate™ GXPS1 analyzer fitted with a 10kV/0.15mA Sn X-ray source using approximately 1g of dried and milled powder for the measurement.

[075] In this specification, particle size (equivalent spherical diameter) distribution and mean size measurements are as measured in a well known manner by sedimentation of a fully dispersed dilute suspension of the particles in a standard aqueous medium using a SEDIGRAPH™ 5100 machine supplied by Micromeritics Corporation.

GENERAL PROCEDURE

[076] A general and typical embodiment of a method of the the present invention is illustrated in Figure 1, which shows the processing involving selective flocculation for beneficiation of a crude kaolin clay. In the following description, percentage by weight values given for additives are, unless otherwise stated, percentages by weight of dry or active amounts of the additives based upon the dry weight of the inorganic particulate material present in the treated suspension.

[077] As seen in Figure 1, crude, particulate kaolin clay obtained from Georgia, USA is delivered as a substantially dry solid material from a source **1** together with water from a source **2** to a blunger **3**. An aqueous suspension having a solids content of at least about 35% by weight, e.g., from about 40% to about 70% or more by weight, is formed in the blunger **3**.

[078] The following ingredients are optionally added to the suspension being treated in the blunger **3**: (a) inorganic dispersant, *e.g.,* sodium hexametaphosphate and/or sodium silicate, from a source **4**; (b) alkali, *e.g.,* sodium hydroxide or sodium carbonate, from a source **5**; and (c) organic polyelectrolyte dispersant, *e.g.,* sodium polyacrylate, from a source **6**. The dispersant may typically comprise about 5 pounds of sodium hexametaphosphate (active basis) per dry ton of clay and/or from about 4 to about 6 pounds of sodium silicate (active basis) per dry ton of clay. The sodium silicate may have a molecular ratio of 3.2 Na_2O:1.0 SiO_2. The sodium hexametaphosphate may have a molecular ratio of 1.1 NaO:1.0 P_2O_5, and may be obtained from Calgon Corporation, Pittsburgh, Pa. In some cases, sodium polyacrylate may also be delivered together with the sodium

hexametaphosphate to the blunger **3**. A base, *e.g.,* sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) may be added to the slurry in the blunger **3** to adjust the pH to a given level.

[079] The materials from the sources **1**, **2**, **4**, **5**, and **6** are thoroughly mixed and worked together in the blunger **3**. Mechanical working of the aqueous suspension of kaolin in the blunger **3** is applied to break down agglomerates of solid particles. The resulting dispersed suspension has a pH of about 6.4 to about 7. An output stream **7** comprising the dispersed suspension after treatment in the blunger **3** is supplied, optionally after dilution with water from a source **8**, to a degritter **9** where large particles, are separated and removed. The dispersed suspension may be passed through a Cowles mixer or similar high shear device to provide liquid working. If utilized, the high shear device is preferably after, rather than before, the degritter **9** in order to reduce wear on the mixing blade.

[080] The degritted kaolin suspension is then delivered to a conditioning tank **11** where the suspension is allowed to stand with gentle mechanical stirring for an ageing period, *e.g.,* for at least 30 minutes, for example, for several hours or days. Before and/or after conditioning by ageing, optional conditioning chemical, *e.g.,* a sodium halide and/or a sodium polycarboxylate, may be added from a chemical additive source **10**. For example, about 5 to 40 pounds (active NaCl) per dry ton of clay with about 20 pounds being typical may be added from source **10**. The sodium chloride may be added to the degritted kaolin suspension through use of static mixers.

[081] The suspension is optionally delivered to a mixer **12**, which may be an in-line static mixer. The suspension may optionally be diluted by addition of water from a source **13** to adjust the specific gravity of the suspension. The pH of the suspension is adjusted to be about 9.5 or greater by addition of alkali such as sodium hydroxide or sodium carbonate from a source **14**. An output stream from the mixer **12** comprising the kaolin suspension plus additives having a low solids concentration for example of

from about 10% to about 15% by weight and a pH of at least about 9.5, such as about 11.5. The suspension is optionally passed through a heater **15** (*e.g.*, a heat exchanger), which heats the suspension to a temperature of ranging from about 30°C to about 40°C.

[082] A stream of the suspension either from the conditioning tank **11** or that has been optionally heated by the heater **15** is delivered to a mixer **17**, which may be an in-line static mixer, where at least one selective flocculation polymer comprising a high molecular weight polyacrylamide/polyacrylic acid polymer added from a source **16**. If the at least one selective flocculation polymer is determined to have a relative anionicity in the range of about 4.5% to about 8%, the polymer is added during continuous mixing of the suspension.

[083] The at least one selective flocculation polymer is selected by a titration process. 100 ml of deionized water and 3.0 ml of polymer solution (0.075% concentration) are added to a 250 ml beaker and allowed to stir for 1 minute. 6.0 ml of 0.001 N polydiallyl dimethylammonium chloride (PolyDADMAC) from BTG Mutek is slowly added to the mixture from a 10 ml burette, and stirring is maintained for an additional minute. 0.15 N NaOH is added dropwise, such that the pH is basic but below about 9.5. 3-4 drops of an indicator solution, such as, for example, toluidine blue, is added to the mixture until a uniform aqua-blue color is achieved. The mixture is then titrated with potassium polyvinyl sulfate (PVSK) from BTG Mutek from a 10 ml burette until the end point is reached; a light violet/purple. The amount of PVSK in ml needed to titrate the mixture is compared against the amount in ml need to titrate a blank and to titrate the standard, such as 346 polymer from NALCO, which has a known anionic charge density of 5.4. The relative anionicity, as measured against the standard is determined by equation 1:

$$\frac{(\text{ml PVSK to titrate blank} - \text{ml PVSK to titrate unknown polymer sample})}{(\text{ml PVSK to titrate blank} - \text{ml PVSK to titrate known sample of 346E polymer})} \times 5.4 = \text{relative anionicit}$$

[084] The output of the mixer **17** is a stream **18** of the suspension which is delivered as a feed to a separator **19** in which separation of kaolinite from impurities by selective flocculation takes place. Following this separation, a flocculated underflow layer **20** and a deflocculated overflow layer **21** are formed. A product stream **23** from the underflow layer **20** comprising beneficiated kaolin flocs is collected from the separator **19** at its base **22**. A waste stream **24** comprising deflocculated impurities separated by the selective flocculation process in the overflow layer **21** is extracted from an upper region of the separator **19**.

[085] The suspension of kaolin in the product stream **23** is passed, optionally after shearing of the flocs therein by a shearing device **25**, through an ozonizer **27** in which ozone gas is applied thereto. The concentration of ozone employed may range from, for example, about 0.01 % to about 0.05% by weight. The ozone breaks down residual polymer and other oxidizable impurities, *e.g.*, organic coloring contaminants, present in the suspension. An output stream **28** from the ozonizer **27** is delivered to a plant **29** in which the beneficiated kaolin suspension is further treated by conventional processing steps, such as bleaching, dewatering, spray drying, etc., to produce a commercially acceptable pigment product **30** available in dry or slurry form as required, *e.g.*, having the properties described earlier.

EXAMPLE

[086] The following Example illustrates the benefits of a method embodying the invention as compared with the prior art. Where a percentage value of an ingredient or additive is stated, this is the percentage by weight on a dry or active basis based on the dry weight of kaolin present in the slurry.

[087] A series of selective flocculation polymers with measured anionicities varying from about 1% to about 17% were studied in suspensions of kaolin clay comprising titania impurities. Each suspension was prepared from the same source of kaolin clay. For each suspension, 200 grams of the dry kaolin clay was diluted with water. The resultant suspensions had a solids

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concentration of about 10%. The pH of each suspension was then adjusted to about 11.5 with a 10% NaOH solution.

[088] For each selective flocculation polymer studied, a solution comprising the selective flocculation polymer was prepared to a 0.075% strength. For example, 2.25 grams of polymer would be dissolved in 3000 grams of water.

[089] Each polymer solution was added slowly to a known volume and weight of the suspension under continuous mixing conditions until flocs were visible. At that point mixing was suspended and the flocs permitted to settle. When the flocs had settled to one half the original volume, the specific gravity of the supernantant was measured by hydrometer. If the specific gravity was greater than 1.004, then flocs were resuspended with mixing and additional polymer solution added. The process was repeated until the specific gravity of the supernatant was 1.004 or less.

[090] The total amount of polymer solution added was recorded. In addition, the time in seconds for the flocs to settle to one half the original volume was recorded. After the supernatant was decanted from the precipitate, the weight percent of titania remaining in the precipitate was recorded.

[091] Figure 2 graphs the recorded remaining titania (weight percent) versus the measured anionicity of the selective flocculation polymer. The graph indicates a possible operating range of approximately 1% to 12% and a narrowed operating range of approximately 6% to 9%. Figure 3 graphs the dosage of selective flocculation polymer used (lbs of polymer/ ton of clay) versus the measured anionicity of the selective flocculation polymer. The graph indicates a possible operating range of approximately 1% to 11% and a narrowed operating range of approximately 4% to 7%. Figure 4 graphs settling times (seconds) the measured anionicity of the selective flocculation polymer. The graph indicates a possible operating range of approximately 1%

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to 10% and a narrowed operating range of approximately 2% to approximately 7%.

[092] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and example be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A method for the treatment of kaolin particulate material comprising:

(a) providing a dispersed aqueous suspension comprising kaolin particulate material and having a pH of at least about 7.5;

(b) selecting at least one selective flocculation polymer, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 1% to about 12%;

(c) selectively flocculating said suspension into a first layer and a second layer by adding to said suspension said at least one selective flocculation polymer; and

(d) separating said first layer from said second layer.

2. A method according to claim 1, wherein said kaolin particulate material comprises a primary kaolin clay.

3. A method according to claim 1, wherein said kaolin particulate material comprises a sedimentary kaolin clay.

4. A method according to claim 1, wherein said kaolin particulate material comprises at least one impurity.

5. A method according to claim 4, wherein said at least one impurity is present in an amount of at least 0.1% by weight, based on the dry weight of the kaolin particulate material.

6. A method according to claim 5, wherein said at least one impurity is chosen from titania, anatase, smectite, iron oxide, and mica.

7. A method according to claim 1, wherein said dispersed aqueous suspension is provided by a process comprising including at least one dispersant with the aqueous suspension of kaolin particulate material.

8. A method according to claim 1, further comprising blunging said dispersed aqueous suspension.

9. A method according to claim 8, wherein said suspension comprises said kaolin particulate material in an amount of at least about 35% by weight, on a dry weight basis, prior to blunging.

10. A method according to claim 8, wherein said suspension comprises said kaolin particulate material in an amount ranging from about 40% to about 70% by weight, on a dry weight basis, prior to blunging.

11. A method according to claim 1, further comprising conditioning said dispersed aqueous suspension by allowing said suspension to age for a period of at least 30 minutes.

12. A method according to claim 11, further comprising conditioning said dispersed aqueous suspension by adding to said suspension at least one conditioning chemical.

13. A method according to claim 12, wherein said at least one conditioning chemical is added after said ageing.

14. A method according to claim 11, further comprising adjusting the pH of said suspension to a pH ranging from about 6.5 to about 7.5 prior to said ageing.

15. A method according to claim 1, wherein said pH is at least about 9.5.

16. A method according to claim 1, wherein said pH is in the range of from about 10.5 to about 12.5.

17. A method according to claim 1, wherein said pH is at least about 11.5.

18. A method according to claim 1, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 4.5% to about 8%.

19. A method according to claim 1, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 6% to about 7%.

20. A method according to claim 1, wherein said at least one selective flocculation polymer is chosen from water-soluble weakly anionic organic polyelectrolytes.

21. A method according to claim 1, wherein said at least one selective flocculation polymer is chosen from polyacrylamide copolymers.

22. A method according to claim 1, wherein said at least one selective flocculation polymer is chosen from polyacrylamide/polyacrylic acid copolymers.

23. A method according to claim 1, wherein said at least one selective flocculation polymer has a molecular weight of at least 100,000.

24. A method according to claim 1, wherein said at least one selective flocculation polymer has a molecular weight of at least 1,000,000.

25. A method according to claim 1, wherein said selecting at least one selective flocculation polymer comprises measuring the measured anionicity value by a titration method.

26. A method according to claim 1, wherein said suspension comprises said kaolin particulate material in an amount ranging from about 10% to about 15% by weight, on a dry weight basis, prior to said selective flocculating.

27. A method according to claim 1, wherein said at least one selective flocculation polymer is present in an amount ranging from about 0.01% to about 0.5% by weight, based on the dry weight of the kaolin particulate material.

28. A method according to claim 1, wherein said at least one selective flocculation polymer is added to said suspension in the form of a solution comprising said at least one polymer.

29. A method according to claim 28, wherein said at least one selective flocculation polymer is present in the solution at a concentration ranging from about 0.025% to about 0.25%.

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30. A method according to claim 28, wherein said at least one selective flocculation polymer is present in the solution at a concentration of about 0.075%.

31. A method according to claim 1, wherein said second layer has a specific gravity ranging from about 1.001 to about 1.030

32. A method according to claim 1, wherein said second layer has a specific gravity ranging from about 1.001 to about 1.004.

33. A method according to claim 1, wherein said selective flocculating comprises mixing said suspension.

34. A method according to claim 1, further comprising redispersing said separated flocculated product layer and then selectively flocculating said redispersed layer.

35. A method for the treatment of kaolin particulate material comprising:

(a) providing a dispersed aqueous suspension of said kaolin particulate material having a pH of at least about 7.5;

(b) selecting at least one selective flocculation polymer, wherein said at least one polymer has a narrow range of variability for measured anionicity and has a measured anionicity ranging from about 1% to about 12%;

(c) selectively flocculating said suspension with adjusted pH into a first layer and a second layer by adding to said suspension said at least one polymer; and

(d) separating said first layer from said second layer.

36. A method according to claim 35, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 4.5% to about 8%.

37. A method according to claim 35, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 6% to about 7%.

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38. A method for the treatment of kaolin particulate material comprising:

(a) providing a dispersed aqueous suspension of said kaolin particulate material having a pH of at least about 7.5;

(b) selecting at least one selective flocculation polymer, wherein said at least one selective flocculation polymer has been manufactured by a continuous process and has a measured anionicity ranging from about 1% to about 12%;

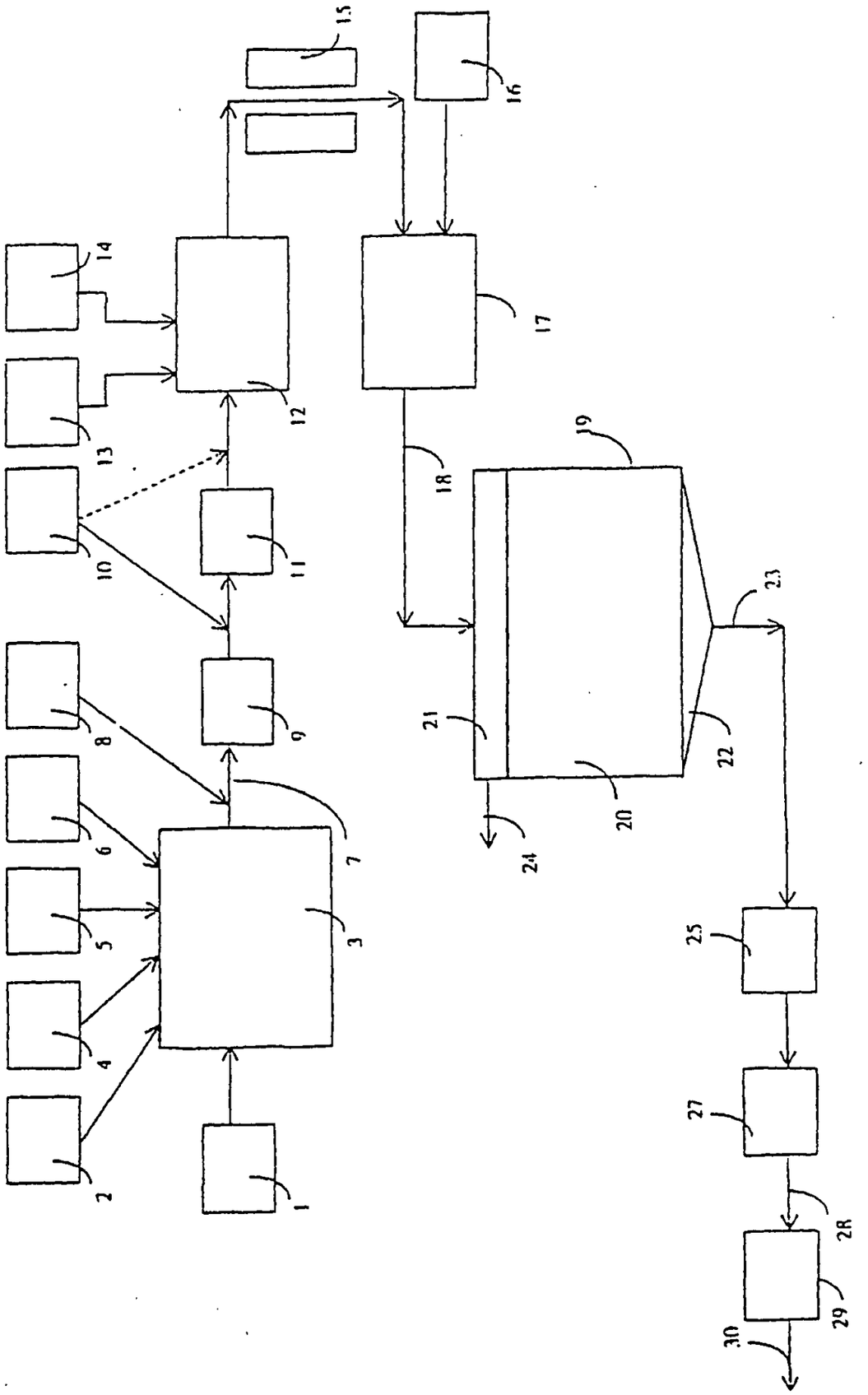
(c) selectively flocculating said suspension with adjusted pH into a first layer and a second layer by adding to said suspension said at least one selective flocculation polymer; and

(d) separating said first layer from said second layer.

39. A method according to claim 38, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 4.5% to about 8%.

40. A method according to claim 38, wherein said at least one selective flocculation polymer has a measured anionicity ranging from about 6% to about 7%.

Figure 1



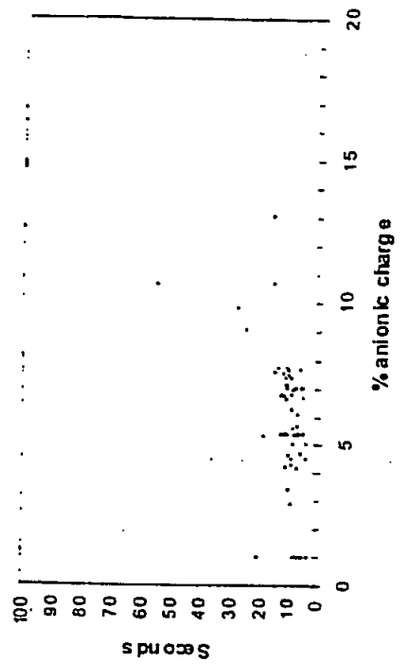


Figure 4

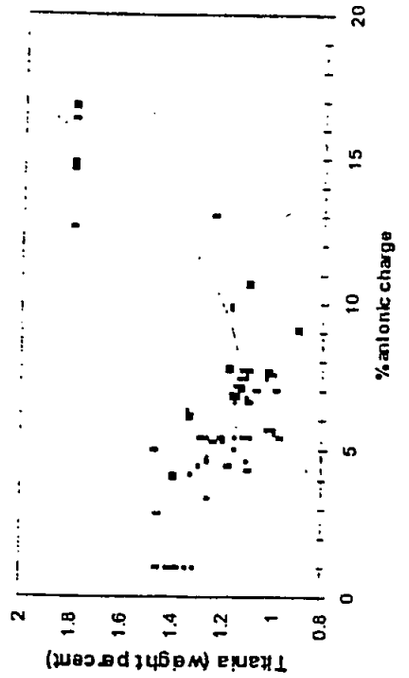


Figure 2

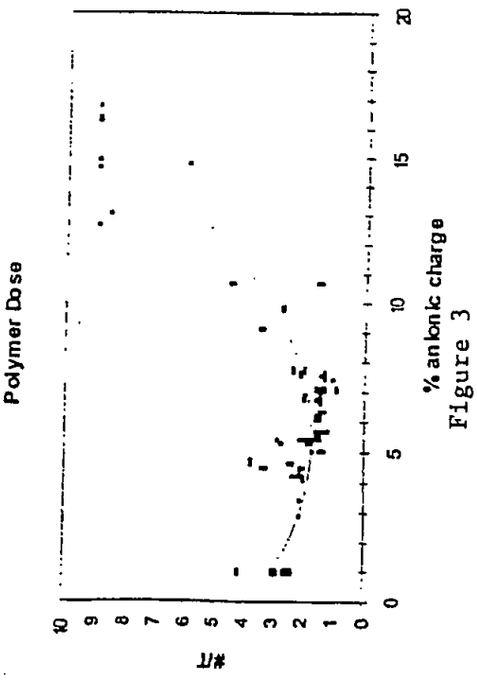


Figure 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/002011

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B33/04 C04B33/10 B01D21/01

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)
IPC 7 C04B B01D C02F

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)
EPO-Internal, WPI Data, PAJ, CHEM ABS Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/68160 A (GREENHILL DAVID A ; IMERYS PIGMENTS INC (US); MAY ANTHONY ALLAN (US);) 16 November 2000 (2000-11-16) page 4, line 23 - page 5, line 9 page 12, line 16 - page 13, line 4 example 1	1-40
X	US 3 837 482 A (SHERIDAN J) 24 September 1974 (1974-09-24) cited in the application claim 1; examples	1-40

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document 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 cited 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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 June 2004	22/06/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Munro, B

Form PCT/ISA/210 (second sheet) (January 2004)

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/002011

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to clai
X	PRADIP ET AL.: "Selective Flocculation of Kaolinite from Mixtures with Tribasic Calcium Phosphate Using Hydrolysed Polyacrylamides" INTERNATIONAL JOURNAL OF MINERAL PROCESSING, vol. 31, 1991, pages 259-270, XP009032071 AMSTERDAM page 265 - page 268	1-40
P,X	WO 03/024888 A (IMERYS PIGMENTS INC) 27 March 2003 (2003-03-27) paragraph '0048!; examples	1-40
P,X	WO 03/089524 A (PRING GRAHAM M ; IMERYS PIGMENTS INC (US); GOLLEY CHRISTOPHER R L (US)) 30 October 2003 (2003-10-30) paragraph '0034! - paragraph '0035!; example 1	1-40

Form PCT/ISA/210 (continuation of second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2004/002011

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0068160 A	16-11-2000	AU 763786 B2	31-07-2003
		AU 4822700 A	21-11-2000
		BR 0010346 A	19-02-2002
		CA 2370506 A1	16-11-2000
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US 3837482 A	24-09-1974	NONE	
WO 03024888 A	27-03-2003	US 2003141224 A1	31-07-2003
		CA 2452477 A1	27-03-2003
		WO 03024888 A1	27-03-2003
WO 03089524 A	30-10-2003	WO 03089524 A1	30-10-2003

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 10109100
PUBLICATION DATE : 28-04-98

APPLICATION DATE : 04-10-96
APPLICATION NUMBER : 08264344

APPLICANT : TERUNAITO:KK;

INVENTOR : NISHIMURA HIROYUKI;

INT.CL. : C02F 11/14 B01D 21/01 B01F 17/52 C02F 11/06 C02F 11/08

TITLE : VOLUME REDUCTION TREATMENT OF HIGH WATER CONTAINING DREADING BOTTOM MUD

ABSTRACT : PROBLEM TO BE SOLVED: To provide the volume reduction treatment method of high water containing dredging bottom mud suitable to a massive treatment, capable of flocculating the dredging bottom mud without adversely affecting environment and also capable of using a general low pressure dehydrator.

SOLUTION: Sodium polyacrylate 3,000,000 to 5,000,000 in weight average molecular weight and 25-75% in neutralization degree is added to the high water containing dredging bottom mud having a 400-3000% water content ratio to make the dispersion stable, and next a divalent or a trivalent metallic salt aqueous solution is added to form hydrophobic flocks and then the flocks are dehydrated naturally or forcedly, thus the volume of the high water containing dredging bottom mud is reduced.

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(19)日本国特許庁（ＪＰ）　(12)**公開特許公報**（Ａ）　(11)特許出願公開番号

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(51)Int.Cl.[6]		識別記号	FI		
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Ｂ０１Ｄ	21/01	１０２	Ｂ０１Ｄ	21/01	１０２
Ｂ０１Ｆ	17/52		Ｂ０１Ｆ	17/52	
Ｃ０２Ｆ	11/06	ＺＡＢ	Ｃ０２Ｆ	11/06	ＺＡＢＡ
	11/08			11/08	

審査請求　未請求　請求項の数５　ＯＬ　（全５頁）

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(54)【発明の名称】　高含水浚渫底泥の減容化処理方法

(57)【要約】
【課題】　本発明は、浚渫底泥を環境に悪影響を与えることなく凝集させ、かつ、汎用、低圧脱水機を使用でき、大量処理に適する高含水浚渫底泥の減容化処理方法を提供する。
【解決手段】　本発明は、含水比４００～３０００％の高含水浚渫底泥に重量平均分子量３００万～５００万、中和度２５％～７５％のポリアクリル酸ソーダを加えて分散安定化をはかり、つぎに二価または三価の金属塩水溶液を加えて疎水性フロックをつくり、しかるのちに、自然または強制的に脱水して高含水浚渫底泥を減容化する方法に関する。

【特許請求の範囲】

【請求項１】　含水比４００％～３０００％の高含水浚渫底泥に重量平均分子量３００万～５００万、中和度２５～７５％のポリアクリル酸ソーダを加えて分散安定化をはかり、つぎに二価または三価の金属塩水溶液を加えて疎水性フロックをつくり、しかるのちに、自然または強制的に脱水することからなる高含水浚渫底泥の減容化処理方法。

【請求項２】　上記ポリアクリル酸ソーダの添加量が、上記高含水浚渫底泥中の浚渫底泥無水物１００グラムあたり１～７グラムの添加率であることを特徴とする請求項１に記載の高含水浚渫底泥の減容化処理方法。

【請求項３】　上記金属塩水溶液として含硫酸基ポリ塩化アルミニウム水溶液または硫酸アルミニウム水溶液を用いることを特徴とする請求項１に記載の高含水浚渫底泥の減容化処理方法。

【請求項４】　上記高含水浚渫底泥として、酸化剤を用いて高含水浚渫底泥中の還元性物質を酸化したものを用いることを特徴とする請求項１に記載の高含水浚渫底泥の減容化処理方法。

【請求項５】　上記酸化剤として、空気、酸素、オゾン、過酸化水素、次亜塩素酸ソーダを用いることを特徴とする請求項４に記載の高含水浚渫底泥の減容化処理方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、湖沼や河川、港湾などから得られる高含水浚渫底泥を、環境への影響を最小限にとどめつつ、凝集、脱水して減容化する方法に関する。

【０００２】

【従来の技術】湖沼や河川、港湾などの底には、多くの場合、ヘドロ状の物質が沈殿、堆積しているが、それらは、栄養塩に富むヘドロ状物質である場合が多く、そこから溶け出る窒素、りんなどの富栄養素が植物プランクトンの異常発生やメタンガス発生の原因となって、著しい環境悪化をもたらしている。汚染の進んだ湖沼や河川、港湾の浄化の有力な方法の一つは、この栄養塩に富むヘドロ状物質を浚渫して取り除くことであり、国や多くの地方自治体がはやくからこれに取り組んで一定の成果を収めているが、その方法は、浚渫船から送られるヘドロを処理ヤードにためて天日乾燥するものが殆どで、処理ヤードに大規模な築堤工事が必要な上、乾燥が終ってヤードを再利用することが可能になるまで長期間（１年以上）を要することから、処分地の確保に頭を悩ませているところがほとんどである。

【０００３】天日乾燥は時間がかかる上、乾燥後といえども処分地に地耐圧が出ず、処分地の用途が制限されることから、無薬注のまま、あるいは、アクリルアミド系の凝集剤を加えて機械脱水する方法も一部で採用されている。すなわち、従来は、湖沼や河川、港湾などから得られる高含水浚渫底泥を減容化処理するにあたっては、底泥を浚渫船で浚渫して堤防で取り囲んだ囲繞堤内に送り、そこで天日乾燥する方法が、あるいは、ポリアクリルアミド系の凝集剤を加えて凝集させてから脱水機にかけ減容化する方法が、もっぱら取られてきた。

【０００４】しかし、アクリルアミド系の凝集剤は、残留するアクリルアミドモノマーの毒性の問題から、自然界で大量に使用することは好ましいことでなく、例えば、厚生省環境衛生局水道課編の「浄水場排水処理施設の手引き」によれば、浄水工程でのアクリルアミド系の凝集剤の使用を禁じている。したがって、特に、湖沼のような閉鎖系水域や、下流に上水道の取り入れ口のあるような河川でのアクリルアミド系の凝集剤の使用は、できるだけ避けることが望ましい。また、無薬注のまま、あるいは、少量のアクリルアミド系の凝集剤を加えて機械脱水する方法は、いずれも脱水に高圧を要するので、高圧フィルタープレス以外、適する脱水方法がない。高圧フィルタープレスは、連続操作ができないから、処理能力が小さく、大量処理に向かない。

【０００５】

【発明が解決しようとする課題】本発明は、浚渫底泥を環境に悪影響を与えることなく凝集させ、かつ、汎用、低圧脱水機を使用でき、大量処理に適する高含水浚渫底泥の減容化処理方法を提供する。

【０００６】

【課題を解決するための手段】本発明は、含水比４００～３０００％の高含水浚渫底泥に重量平均分子量３００万～５００万、中和度２５～７５％のポリアクリル酸ソーダを加えて分散安定化をはかり、つぎに二価または三価の金属塩水溶液を加えて疎水性フロックをつくり、しかるのちに、自然または強制的に脱水して高含水浚渫底泥を減容化する方法に関する。

【０００７】

【発明の実施の形態】本発明の対象となる高含水浚渫底泥の含水比は、４００％～３０００％である。４００％未満の含水比では、たとえ凝集処理できたとしても自由水が少なく、脱水機で分離水を全く得られないか、得られてもごくわずかであり、減容化のメリットはない。３０００％をこえる含水比のものは、通常の浚渫作業でほとんど発生しないし、もし３０００％をこえる含水比のものを本発明の処理法で処理しても、得られるフロックの強度が弱く脱水作業が困難である。本発明でいう含水比（％）とは、汚泥乾燥物重量（固形分）に対する水の重量比に１００をかけた値をいう。含水量は、ＪＩＳＡ－１２０３「土の含水量試験方法」に従って測定する。本発明では、アクリル酸ソーダおよび二価または三価の金属塩の添加量を浚渫底泥無水物の重量に対する重量または容量として記載する。この浚渫底泥無水物の重量は、含水比の測定値から計算によって得ることができ

る。

【０００８】本発明で使用するポリアクリル酸ソーダは、厚生省令第３２号により食品添加物に指定されている安全性の高い物質で、アクリルアミド系の高分子物質と違って環境への影響は指摘されていない。ポリアクリル酸ソーダは、それ自体、凝集性を有し、魚肉練製品・缶詰等の製造時、水溶性魚肉蛋白質廃液にポリアクリル酸ソーダを添加することにより、魚肉蛋白質の回収・再利用及び廃水の浄化に広く使用されているが、この場合のようにポリアクリル酸ソーダを凝集剤として用いる場合の添加量は、５０～２００ｐｐｍ程度と、非常に小さな添加率である。

【０００９】しかし、本発明においては、ポリアクリル酸ソーダを凝集剤として使用するものではない。むしろ、懸濁液にポリアクリル酸ソーダを純分換算で浚渫底泥無水物１００グラムあたり２～７グラムという高い添加率で加えることにより、懸濁粒子にポリアクリル酸ソーダが過剰に吸着され、または、多分子系吸着に伴う表面荷電の逆転、親水性の増大などによって保護コロイド作用の形をとるため、粒子はかえって分散して安定化する。ポリアクリル酸ソーダを所定量加えた段階では、浚渫底泥は凝集状態ではなく、高粘度で、かつ、安定な分散液状態にある。

【００１０】つぎに、この安定分散液に二価または三価の金属塩水溶液を加えて撹拌すると、ポリアクリル酸ソーダが、その内部に懸濁粒子を含んだまま凝集し、疎水性フロックをつくる。本発明で用いるポリアクリル酸ソーダは、重量平均分子量が３００万～５００万のポリアクリル酸ソーダである。ポリアクリル酸ソーダの分子量が極めて大きいため、二価または三価の金属塩水溶液を加えて得られる凝集物は、極めて強度が強く疎水性に富んでいる。凝集物の脱水性の良否を簡単に知る手段として、それを片手で握った時、指の間から凝集物が漏れだしてくるか否かをみる方法がよく使われるが、本発明で得られた凝集物は、指の間から凝集物が漏れることなく、水だけが滲み出る。すなわち、片手で簡単に絞ることができ、極めて脱水性に優れていることが分かる。

【００１１】したがって、これを脱水機にかけると、低含水率のスラッジを得ることができる。処理対象の浚渫底泥の含水比が９００％以上では、野積みによる自然脱水でも脱水、減容化が期待できるし、袋詰め脱水などの簡易強制脱水法を用いて脱水、減容化を行ってもよい。機械脱水法を採用する場合、汎用の低圧脱水機、例えば、スクリュープレス、ベルトプレス、ロールプレス、デカンターなどの連続式の脱水機が使用でき、高圧フィルタープレスに限定される無薬注脱水方式と違って、大量処理が可能である。

【００１２】ポリアクリル酸ソーダを高い添加率で加えて懸濁粒子を分散安定化させた後、二価または三価の金属塩水溶液を加えることで、懸濁粒子とポリアクリル酸ソーダを一緒に凝集させ、高強度、高脱水性のスラッジを得る技術は、今まで存在しなかったものである。

【００１３】本発明で用いるポリアクリル酸ソーダは、重量平均分子量が３００万～５００万のポリアクリル酸ソーダである。重量平均分子量が３００万未満では、強いフロックが得られず、脱水工程から得られる分離水が濁ることが多い。重量平均分子量が５００万をこえると、水に対する溶解性が減少し、効果が減退する。

【００１４】本発明で用いるポリアクリル酸ソーダは、中和度が２５～７５％のポリアクリル酸ソーダである。ポリアクリル酸ソーダの中和度は、医薬品添加物規格（１９９４年追補）ＡＭ－１０５「ポリアクリル酸部分中和物」により測定する。中和度が２５％未満でも疎水性に富んだ凝集物を得ることはできるが、水に対する溶解度が小さく、添加量が多くなって経済的でない。また、中和度が７５％をこえるものでも、おなじく疎水性に富んだ凝集物を得ることはできる。しかし、浚渫底泥中に含まれる溶解性重金属類の吸着力が弱く、例えば、浚渫底泥中に鉄が含まれていると、分離水が、数日後、酸化鉄の赤色を帯びる。中和度が２５～７５％のポリアクリル酸ソーダを用いれば、溶解性重金属類を吸着して沈殿するから、分離水が着色する恐れがない。湖沼の浚渫を計画する際、かえって、ヘドロ中の重金属が溶けだし、水を汚染するとして問題になるケースがあるが、本発明のように、中和度が２５～７５％のポリアクリル酸ソーダを使用して処理すれば、重金属の固定化がおこるので、水を汚染させるおそれはない。

【００１５】本発明で用いるポリアクリル酸ソーダは、通常、粉末品が用いられるが、脱水ケーキの中に油が残ることが許される場合は、油中水型エマルジョン、または、油溶性ポリマーを溶かした高粘性油にポリアクリル酸ソーダ粒子を担持させたものを使うと、反応に要する時間を短縮できる。

【００１６】本発明で用いるポリアクリル酸ソーダの添加量は、浚渫底泥無水物１００グラムあたり１～７グラムである。１グラム未満では、丈夫な凝集物が得られず、また、７グラムをこえても効果には影響ないが、経済的でない。

【００１７】本発明で用いる金属塩は、二価または三価の水溶性金属塩である。一価の金属塩では、ポリアクリル酸ソーダの凝集が起きず、四価以上の水溶性金属塩で汎用のものはないからである。本発明で用いる二価または三価の金属塩としては、たとえば、ポリ塩化アルミニウム、含硫酸基ポリ塩化アルミニウム、ポリ硫酸アルミニウム、塩基性塩化アルミニウム、硫酸アルミニウム、硫酸第一鉄、硫酸第二鉄、塩化第二鉄、アンモニウム明バン、アルミン酸ナトリウム、塩素化コッパラス、塩化亜鉛、硫酸亜鉛が挙げられる。このうち、特に、含硫酸基ポリ塩化アルミニウム、硫酸アルミニウムなどの酸性塩が効果的、かつ、安全、安価であるが、必要に応じ、

塩化カルシウム、塩化マグネシウムなどの中性塩を酸性塩とブレンドして用いてもよい。二価または三価の金属塩水溶液として含硫酸基ポリ塩化アルミニウム（ＰＡＣ）（アルミナ１０～１１％品）水溶液または硫酸アルミニウム（ＡＳ）（アルミナ８．０～８．２％品）水溶液を用いたときの添加量は、浚渫底泥無水物重量に対し、２容量％～１０容量％である。２容量％未満では凝集が不完全であり、１０容量％をこえると、分離液のｐＨが下がりすぎたり、分離液中の塩分濃度が上がり過ぎたりして、分離液の放流に障害となる。含硫酸基ポリ塩化アルミニウムは、ＪＩＳ　Ｋ１４７５に準拠するもの、硫酸アルミニウムは、ＪＩＳ　Ｋ１４５０に準拠するものを使用するのが一般的である。二価または三価の金属塩のかわりにカチオン系の高分子凝集剤を使用しても凝集物は得られるが、カチオン系の高分子凝集剤は毒性があり、本発明の目的にそぐわない。

【００１８】浚渫底泥は、普通、大量の有機物を含んでおり、内部は、著しい還元状態にある。嫌気性菌が繁殖し、ひどい腐敗臭がする場合も珍しくない。このような浚渫底泥であっても本発明の処理法で処理可能であるが、還元状態は、使用するポリアクリル酸ソーダの必要添加量に影響を与える。還元状態の程度は、ＯＲＰ計を用いて酸化還元電位を測定することで知ることができる。酸化還元電位（Ｖ）が負で、その絶対値が大きいほど、著しい還元状態にあり、ポリアクリル酸ソーダの必要量が多くなる。したがって、経済的な処理を考えたとき、あらかじめ、酸化剤を用いて浚渫底泥を酸化してから処理に供するほうが有利な場合がある。

【００１９】酸化剤として、空気、酸素、オゾンなどの酸素類、過酸化水素などの過酸化物、次亜塩素酸ソーダなどの酸素酸塩類が使用できる。空気、酸素、オゾンの場合は、気体を直接吹き込んで撹拌し、過酸化水素水、次亜塩素酸ソーダ水溶液の場合は、薬注ポンプを用いて添加撹拌する。添加量は、浚渫底泥の還元状態の程度で異なるから、ＯＲＰ計を用いて酸化還元電位を測定して添加量を決定する。空気を吹き込むかわりに、浚渫底泥を大気中で激しく撹拌するなどして空気との接触をはかってもよい。

【００２０】

【実施例】本発明を実施例１～４および比較例１～２により詳細に説明する。しかし、本発明はこれに限定されるものではない。

実施例１

含水比７００％の湖水浚渫底泥重量に対し、重量平均分子量５００万、中和度５０％ポリアクリル酸ソーダ粉末を０．５重量％（湖水浚渫底泥無水物重量に対して４重量％）加え、つぎに含硫酸基ポリ塩化アルミニウム水溶液（アルミナ１０～１１％品）を０．７容量％（湖水浚渫底泥無水物重量に対して５．６容量％）加えて疎水性フロックをつくった。これをスクリュープレスを使って脱水した。脱水後のケーキの含水比は２２３％であった。また、分離水の性質と減容率は表１の通りであった。

【００２１】実施例２

含水比９００％の湖水浚渫底泥重量に対し、重量平均分子量５００万、中和度５０％ポリアクリル酸ソーダ粉末を０．３重量％（湖水浚渫底泥無水物重量に対して３重量％）加え、つぎに含硫酸基ポリ塩化アルミニウム水溶液（アルミナ１０～１１％品）を０．４５容量％（湖水浚渫底泥無水物重量に対して４．５容量％）加えて疎水性フロックをつくった。これをベルトプレスを使って脱水した。脱水後のケーキの含水比は２４１％であった。また、分離水の性質と減容率は表１の通りであった。

【００２２】実施例３

含水比１２００％の湖水浚渫底泥重量に対し、重量平均分子量５００万、中和度５０％ポリアクリル酸ソーダ粉末を０．２５重量％（湖水浚渫底泥無水物重量に対して３．２５重量％）加え、つぎに硫酸アルミニウム水溶液（アルミナ８．０～８．２％品）を０．３２容量％（湖水浚渫底泥無水物重量に対して４．２容量％）加えて疎水性フロックをつくった。これを遠心分離器にかけて２０００回転で５分間脱水した。脱水後のケーキの含水比は２６０％であった。また、分離水の性質と減容率は表１の通りであった。

【００２３】実施例４

含水比１２００％の湖水浚渫底泥１リットルをビーカーに取り、４枚羽根のスクリュー撹拌機で５０分間激しく撹拌した。ＯＲＰ計による酸化還元電位は、撹拌前－３４ｍＶ、撹拌後＋１１５ｍＶであった。これに、重量平均分子量５００万、中和度５０％ポリアクリル酸ソーダを０．２重量％（湖水浚渫底泥無水物重量に対して１．９５重量％）加え、つぎに硫酸アルミニウム水溶液（アルミナ８．０～８．２％品）を０．２６容量％（湖水浚渫底泥無水物重量に対して３．３容量％）加えて疎水性フロックをつくった。これを遠心分離器にかけて２０００回転で５分間脱水した。脱水後のケーキの含水比は２５３％であった。

【００２４】比較例１

含水比７００％の湖水浚渫底泥３００ｍｌをフィルタープレスに送って３気圧で３０分間脱水した。脱水後のケーキの含水比は１７０％、ケーキ容積は７２ｍｌであった。また、分離水の性質と減容率は表１の通りであった。フロックが弱いため、フィルタープレス以外の汎用脱水機では脱水できなかった。

【００２５】比較例２

含水比７００％の湖水浚渫底泥３００ｍｌに、０．２重量％のアクリルアミド系高分子凝集剤（重量平均分子量５００万）溶液を３．５ｍｌ（この湖水浚渫底泥無水物に対して高分子純分換算で０．０２重量％に相当）加えて反応させた後、フィルタープレスに送って３気圧で１

０分間脱水した。脱水後のケーキの含水比は１８９％、ケーキ容積は７７ｍｌであった。また、分離水の性質と減容率は表１の通りであった。フロックが弱いため、フィルタープレス以外の汎用脱水機では脱水できなかった。

【００２６】実施例１～４および比較例１～２の結果を表１に示す。表１において、透過率は、３５０ｎｍの波長の光の透過率を、蒸留水を１００％として表した値である。測定は、日立の１００－６０型ダブルビーム分光光度計によりおこなった。また、減容率は、供試浚渫底泥容積に対する脱水後のケーキ容積の割合（％）を１００から引いた値を示した。

【表１】

	分離水の性質					減容率 (%)
	pH	COD (mg/l)	Fe (mg/l)	Al (mg/l)	透過率 (%)	
実施例１	5.6	13	不検出	不検出	96.5	60
実施例２	5.8	15	0.1	1.9	96.0	66
実施例３	5.9	14	0.5	3.7	93.2	72
比較例１	6.8	11	1.5	0.3	96.8	66
比較例２	7.1	18	1.8	0.4	95.4	64

【００２７】

【発明の効果】実施例１～３から明らかなように、本発明の処理法によれば、浚渫底泥を環境に悪影響を与えることなく凝集させ、かつ、汎用、高能力の低圧脱水機することにより、容積を２８／１００～４０／１００にまで減らせることが分かる。また、実施例３と実施例４の比較から、浚渫底泥を酸化することから薬注量を減らせることがわかる。一方、比較例のように無薬注、あるいは、少量のアクリルアミド系高分子凝集剤で処理しても、得られるフロックは弱く、高圧フィルタープレス以外の脱水機は、使用できないことが分かる。

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(54) METHOD FOR TREATING DREDGED MATERIAL

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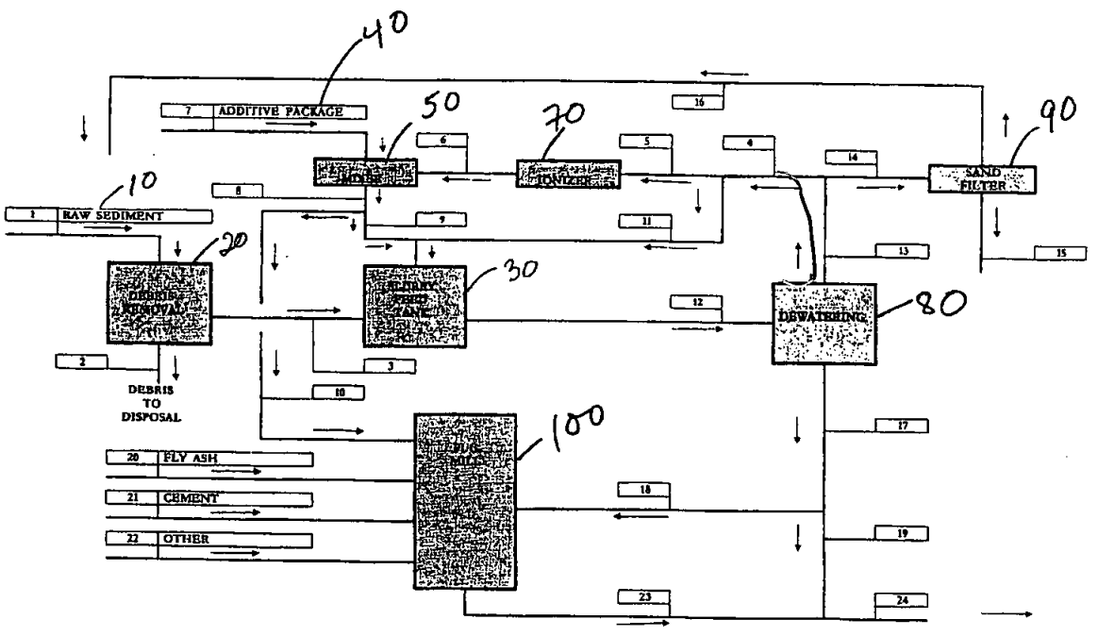
(57) **ABSTRACT**

The present invention provides a method for treating dredged material in which liquid is first added to the dredged material, and dewatering the dredged material to obtain a filtrate and a solid portion. Contaminants are removed from the dredged material by at least one oxidation process. The solid portion may be used to form structural articles.



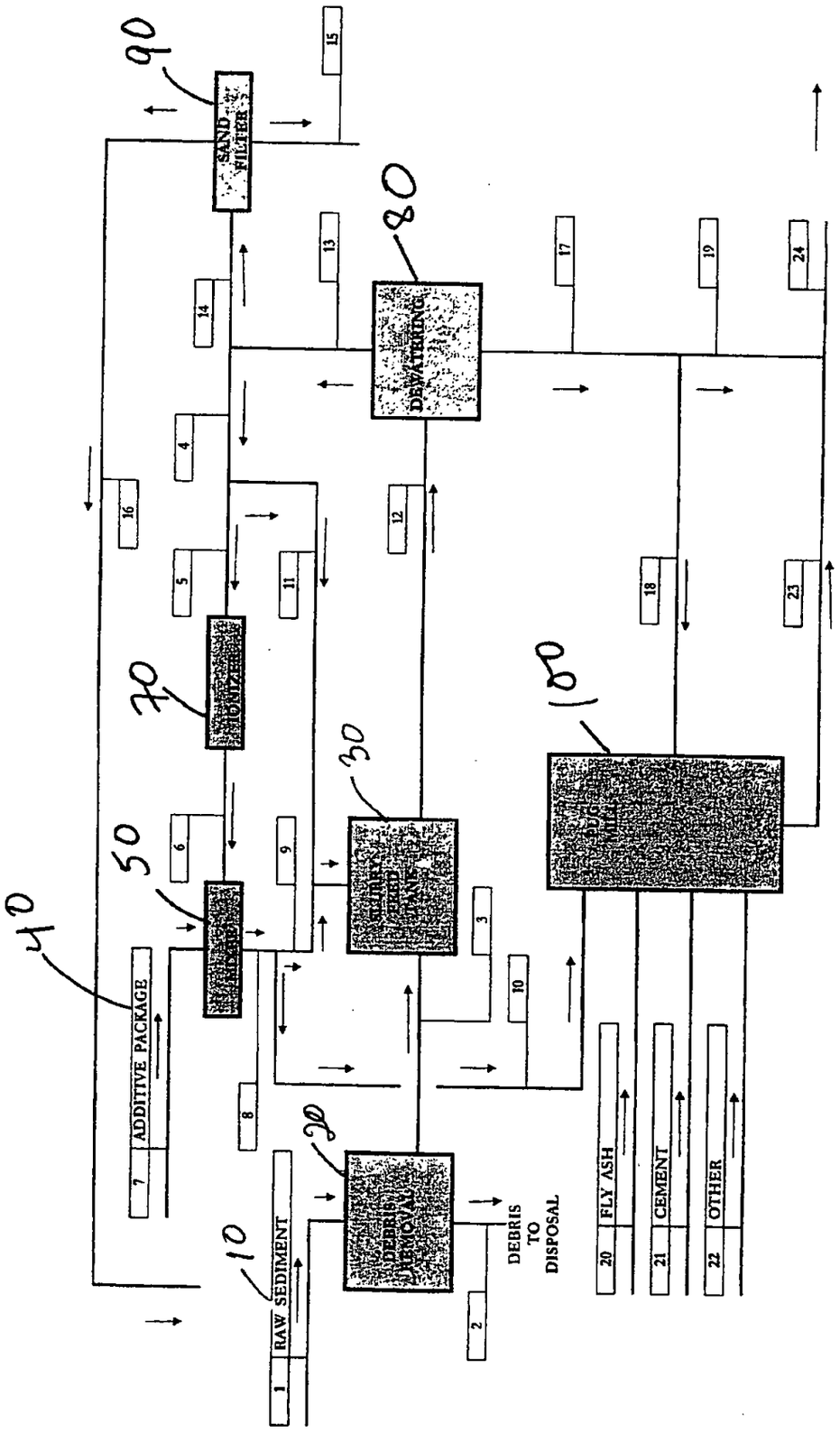


Figure 1

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STREAM	1	2	3	4	5	6	7	8	9	10	11	12
DESCRIPTION	RAW SEDIMENT FROM BARGE TO MTC	DEBRIS TO DISPOSAL	RAW SEDIMENT FROM BARGE LESS DEBRIS	TOTAL RECYCLE FILTRATE WATER	RECYCLE FILTRATE WATER TO IONIZER	IONIZED WATER FROM IONIZER TO MIXER	ADDITIVE PACKAGE TO MIXER	MIXER OUTLET	MIXER OUTLET TO SLURRY TANK	MIXER OUTLET TO MINI MILL	RECYCLE FILTRATE WATER TO SLURRY TANK	SLURRY FEED TO DEWATERING
	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR
DRY SEDIMENT	33,783.8	2,079.0	31,704.8	11.0	0.3	0.3		0.3	0.3	-	10.7	31,818.8
WATER	70,166.3		70,166.3	110,139.0	2,676.3						107,462.7	180,305.2
DECON CHEMICAL ADDITIVES:												
OXIDANT							79.3	79.3	79.3	-		
IONIZED WATER						2,676.3		2,676.3	2,676.3	-		
DEWATERING POLYMER							23.8	23.8	23.8	-		
BENEFICIAL USE ADDITIVES:												
FLY ASH												
CEMENT												
OTHER												
TOTAL	103,950.0	2,079.0	101,871.0	110,150.0	2,676.6	2,676.6	103.0	2,779.6	2,779.6	-	107,473.4	212,124.0
BULK DENSITY:												
STREAM, # / CF	77.0	80.0	76.9	64.0	64.0	64.0	65.5	65.5	65.5		64.0	69.6
VOLUME FLOW												
GPM	168.3		165.1	214.6	5.2	5.2	0.2	5.3	5.3		209.3	379.8
CY/HR	50.0	1.0	49.0	63.7	1.5	1.5	0.1	1.6	1.6		62.2	112.8
WT% SOLIDS	32.500%		31.122%	0.010%	0.010%	0.010%	100.000%	3.717%	3.717%		0.010%	15.000%
WT% WATER	67.500%		68.878%	99.990%	99.990%	99.990%	0.000%	96.283%	96.283%		99.990%	85.000%
WT% WATER / WT% SOLIDS * 100%	207.7%		221.3%									
OXIDANT, PPM OF DRY SEDIMENT												
POLYMER, # PER TON OF DRY SEDIMENT												
WATER REMOVED:												
GALLONS PER CY OF RAW SEDIMENT												
% OF RAW SEDIMENT VOLUME												
FLY ASH ADDED AS % OF DEWATERED SEDIMENT												
CEMENT ADDED AS % OF DEWATERED SEDIMENT												
FLY ASH ADDED IN # PER CY OF RAW SEDIMENT												
CEMENT ADDED IN # PER CY OF RAW SEDIMENT												

Figure 2(a)

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STREAM	13	4	14	15	16	17	18	19	20	21	22	23	24
DESCRIPTION	TOTAL FILTRATE WATER	TOTAL RECYCLE FILTRATE WATER	PRODUCT FILTRATE WATER TO SAND FILTER	PRODUCT FILTRATE WATER FROM SAND FILTER	SEDIMENT CAPTURED ON SAND FILTER	DEWATERED SEDIMENT FROM DEWATERING	DEWATERED SEDIMENT TO PUG MILL MILL	DEWATERED SEDIMENT TO BENEFICIAL USE	FLY ASH ADDED TO PUG MILL	CEMENT ADDED TO PUG MILL	OTHER ADDED TO PUG MILL	BENEFICIAL USE PRODUCT FROM PUG MILL	TOTAL BENEFICIAL USE PRODUCT
	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR	# / HR
DRY SEDIMENT	15.6	11.0	4.6	1.4	3.2	31,803.2	31,803.2	-				41,288.4	31,803.2
WATER	156,313.3	110,139.0	46,174.3	46,174.3	0.0	23,991.9	23,991.9	-				22,039.3	23,991.9
DECON CHEMICAL ADDITIVES:													
OXIDANT													
IONIZED WATER													
DEWATERING POLYMER													
BENEFICIAL USE ADDITIVES:													
FLY ASH									5,579.5				
CEMENT										1,952.8			
OTHER											-		
TOTAL	156,328.9	110,150.0	46,178.9	46,175.7	3.2	55,795.1	55,795.1	-	5,579.5	1,952.8	-	63,327.5	55,795.1
BULK DENSITY:													
STREAM, # / CF	64.0	64.0	64.0	64.0	100.0	92.4	92.4		45.0	90.0		84.5	89.2
VOLUME FLOW													
GPM	304.5	214.6	90.0	89.9	0.0	75.3	75.3		15.5	2.7		93.5	78.0
CY/HR	90.5	63.7	26.7	26.7	0.0	22.4	22.4		4.6	0.8		27.8	23.2
WT% SOLIDS	0.010%	0.010%	0.010%	0.003%	100.000%	57.000%	57.000%					65.198%	57.000%
WT% WATER	99.990%	99.990%	99.990%	99.997%	0.000%	43.000%	43.000%					34.802%	43.000%
WT% WATER / WT% SOLIDS * 100%													
OXIDANT, PPM OF DRY SEDIMENT													
POLYMER, # PER TON OF DRY SEDIMENT													
WATER REMOVED:													
GALLONS PER CY OF RAW SEDIMENT			107.9	107.9									
% OF RAW SEDIMENT VOLUME			53.45%	53.44%									
FLY ASH ADDED AS % OF DEWATERED SEDIMENT									10.00%				
CEMENT ADDED AS % OF DEWATERED SEDIMENT										3.50%			
FLY ASH ADDED IN # PER CY OF RAW SEDIMENT									111.6				
CEMENT ADDED IN # PER CY OF RAW SEDIMENT										39.1			

Figure 2(b)

METHOD FOR TREATING DREDGED MATERIAL

FIELD OF THE INVENTION

[0001] This invention relates to a novel method for treating dredged material in which dredged material is dewatered, contaminants are removed in at least one oxidation process, and the treated dredged material is suitable for beneficial reuse.

BACKGROUND OF THE INVENTION

[0002] Periodic dredging of sea and river ports and channels must be performed in order to maintain safe navigable waterways. Unfortunately, due to pollution of our waterways, the dredged material often contains substances which does not allow easy disposal of the dredged material either at sea, or on land. In addition the dredged material typically includes very finely suspended solids which are difficult to separate from the aqueous suspensions and solidify. Moreover, such material includes finely divided clays, shells and organic matter which is typically not directly usable as landfill material.

[0003] Conventional approaches for treating dredged materials have included settling techniques and dewatering of the dredged material. Unfortunately, settling procedures require extended term periods and often cannot be practically employed in view of the large amounts of material which must be dredged from a waterway or the vast acreage requirements for settling. In addition dewatering can be an expensive and inefficient process. Further, dredged material contaminated with pollutants, even if dewatered cannot be easily disposed of in landfill or at sea without detriment to the environment.

SUMMARY OF THE INVENTION

[0004] Accordingly, there is a need for a method of treating dredged material which can convert dredged material into an environmentally safe substance which is easily disposed of or is suitable for beneficial reuse.

[0005] These and other objects of the invention are obtained by a method for treating a dredged material comprising removing bulk particles from the dredged material, first adding liquid to the dredged material, and thereafter separating liquid from the dredged material to obtain a filtrate and solid portion. Contaminants are removed from the dredged material by subjecting the dredged material to at least one oxidation process. The solid portion may be formed into a structural article.

[0006] Adding water to the dredged material, prior to dewatering, yields a slurry stream that upon dewatering results in a solid portion which is easily processed into a structural article.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] **FIG. 1** is a schematic illustration of an arrangement for treating dredged material in accordance with the invention; and

[0008] FIGS. **2**(*a*) and **2**(*b*) are tables setting forth concentration of liquid and solid materials processed in the arrangement of **FIG. 1**.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] An arrangement for treating dredged material is shown in **FIG. 1**. Raw sediment **10** is obtained from a waterway and loaded onto a vessel or barge. The dredged material may be treated on the barge or vessel itself, or alternatively may be transported to a land based treatment center. Bulk material is removed from the sediment in receptacle **20**. The bulk material or debris which has a particle size of greater than ½ inch, preferably greater than ¼ inch, is removed by one or more vibrating screens. The remaining dredged material which typically has a solids content of 25% to 45%, more typically approximately 35% by weight, is conveyed to slurry tank **30** and liquid is added reducing the solids content to 10% to 20%, preferably 15% by weight.

[0010] If the dredged material contains organic contaminants, oxidizing agents can be included in an additive package **40** which is mixed in a mixer **50** and added to slurry feed tank **30**. Suitable oxidizing agents include but are not limited to the group consisting of oxygen, hydrogen peroxide, ozone, chlorine, chlorine dioxide, sodium hypochlorate, calcium hypochlorate, sodium chlorate, sodium chlorite, bleach, potassium permanganate and mixtures thereof. The amounts of oxidizing agent employed is 100 to 20,000 ppm per ton by weight of dry solids. Suitable oxidizing systems are disclosed in U.S. Pat. No. 5,914,040 which is incorporated by reference herein. Optionally an ionizer **70** can be used to generate oxygen radicals, for example, as disclosed in U.S. Pat. No. 5,587,069 which is also incorporated by reference herein, which also acts as an oxidizing agent.

[0011] The additive package **40** preferably includes a flocculating agent which is a polyelectrolyte. Suitable polyelectrolytes are cationic polyelectrolytes including but not limited to neutral polymers and quaternary polyamines, neutral or quaternary polyalklyeneamines and polyhydroxy alkyleneamines, for example polyethyleneamine, poly (2-hydroxy-1-propyl-N-methylammonium chlorine), poly (2-hydroxy-1-propyl-1-N-dimethylammonium chloride), poly (vinyl-2-imidazolinium hydrogensulphate), poly (diallyldimethylammonium chloride, polyaminoacrylates, polyaminomethacrylates, polyaminodialkyl acrylate), for example poly (N,N-dimethylaminoethyl methacrylate) alone or a copolymer with acrylamide, polyaminacrylamides, polymethylacrylamides, polydialkylacrylamides for example, poly (N,N-dimethylaminopropylmethacrylamide) and poly (N,N-dimethylaminoethylacrylamide). A mixture of polyelectrolytes may be used. A preferred cationic polyelectrolyte flocculating agent is a low charge, high molecular weight polyelectrolyte. Most preferred is a copolymer of a quaternary acrylate salt and acrylamide, Nalco N-9908 dry, available from Ondeo-Nalco located in Midlothian, Va. The flocculating agent is added to the dredged material in the amount of 0.5 to 10 lbs per ton of dry dredged material in slurry feed tank **30**.

[0012] The dredged material is conveyed to a dewatering receptacle **80**. The dewatering receptacle may include at least one of a belt press, filter press or centrifuge. The most preferred method of dewatering the dredged material to obtain a filtrate and solid portion is dewatering with a belt press. The filtrate obtained from dewatering receptacle **80** can be recycled to mixer **50** or slurry feed tank **30**, or can be further purified by passing the filtrate through sand filter **90**.

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[0013] The solid portion can be fed to a pug mill **100** and combined with structural building materials such as fly ash, cement and other materials to form a structural article as described in U.S. Pat. No. 6,293,731 which is incorporated by reference herein.

[0014] In addition, oxidizing agent **22** can be added if contaminants remain present at levels that exceed end use product specifications. The solid portion can be recycled for beneficial re-use. For example, the solid portion can be used as a liner, protective cover, a daily cover or a final cap over a landfill, for strip mine reclamation, paving material for parking lots, airfield construction, road base or the like.

[0015] A mass balance spreadsheet for the arrangement shown in **FIG. 1** is given in FIGS. **2**(*a*) and **2**(*b*) wherein the raw sediment dredged material, after bulk debris removal, includes 31%±0% by weight liquid and 69%±10% by weight solids. As can be seen from FIGS. **2**(*a*) and **2**(*b*), the slurry feed material conveyed to dewatering receptacle **80** includes 15%±5% by weight solids and 85%±5% by weight liquids. After dewatering, the solid portion including 57%±10% by weight solids and 43%±10% by weight liquid, is conveyed to pug mill **100** where it is mixed with fly ash and cement and other structural materials to form a structural article having 65%±10% by weight solids and 35%±10% by weight liquids.

EXAMPLE

[0016] Sediment will be delivered in barges to an unloading platform. Caterpillar 330 long-stick tracked excavators or their equivalent will be utilized for debris removal and sediment transfer. The first excavator will be equipped with "grapples"for the removal of large foreign objects from the sediment. The excavators may be equipped with television monitors to assist the operator when the barge is at a floating level where vision is obstructed. Debris removed during this operation will be placed in roll-off containers that have been strategically placed, possibly on spud barge(s).

[0017] Once gross debris has been removed, the second excavator will be used to remove sediment from the barge. This excavator will be equipped with a hydraulic, or electric submersible pump attached to the bucket of the machine. This pump will be equipped with a slurry gate to aid in producing a pumpable slurry for the dewatering operation. Wash nozzles will be placed near the suction point of the pump to aid in producing workable slurry suitable for mechanical dewatering with belt or filter presses, or centrifuges.

[0018] Sediment will be pumped from the barge over vibratory screening equipment placed atop a mixing tank. The screening unit will consist of a double-deck vibratory screen, or its equivalent. Material greater than ½ inch, preferably greater than ¼ inch in size (plus ¼), i.e. larger size material, which would adversely affect the mechanical dewatering operation, will be removed during this step. The larger size material will be placed in another roll-off container adjacent to the first mixing tank. The debris and larger size material will be sent to a landfill for disposal. Material smaller than the larger size material will drop through the vibratory screen and into an agitated mixing tank for subsequent transfer to storage-mixing tanks prior to processing in the belt or filter presses or centrifuges.

[0019] Progressive cavity sediment feed pumps will pump material from the sediment storage tanks to each of the belt or filter presses or centrifuges. The belt or filter presses or centrifuges will be equipped with one or more batch tanks where a polyelectrolyte flocculating solution will be prepared. This solution will be combined with the sediment when it is pumped from the storage tanks to the belt or filter presses or centrifuges. The flocculating agent will be metered into the sediment depending on sediment flow rates and the percentage and type of solids present in the sediment.

[0020] As the sediment is dewatered in the belt or filter presses or centrifuges, filtrate water will be produced. This filtrate together with wash water produced during the dewatering process will be pumped to storage tanks where most of the residual solids will settle out. These storage tanks will be equipped with mixers, which will be used should solids in these tanks need to be placed in suspension and returned to the dewatering operation. The sediment as delivered in the barge is anticipated to contain solids in the 40±10% weight percent range, and therefore, some filtrate will be pumped to the barge to aid in producing a suitable slurry for the dewatering operation while the balance of the filtrate water will be disposed of in accordance with all applicable government rules and regulations. Prior to disposal, this effluent will be passed through a sand filter and other suitable equipment to reduce suspended solids and to meet all applicable water discharge specifications.

[0021] Filter cake produced during the mechanical dewatering operation will typically exit the belt or filter presses or centrifuges on conveyors that will deliver cake to a pug mill, as necessary, for blending first with an oxidizing solution for further contaminant reduction as required to meet end product specifications, and additives including cement and fly ash to produce a Beneficial Use Product. Fly ash and cement will be stored in silos. The conveyor that feeds filter cake to the pug mill will be equipped with a weighscale to monitor the weight of material being fed to the pug mill. This weighscale will control the amount of oxidant, cement, fly ash and other additives that are mixed with the filter cake. If required, oxidant can also be added to the dilution tank. Suitable oxidants are described herein above. A proportioning pump will control the addition rate of oxidant, and rotary vane feeders (with speed control) at the bottom of the silos will control the addition rate of the additive materials at various feed rates as determined by the Beneficial Use Product specifications.

[0022] The Beneficial Use Product material will exit the pug mill and be conveyed to an area adjacent to the mill where it will be stockpiled and then loaded, by front-end loader, onto rail cars or trucks for shipment to user locations. Alternatively, the Beneficial Use Product may exit the pug mill directly onto rail cars or trucks for shipment to user locations.

[0023] One skilled in the art will understand the method of the invention can be carried out in a continuous or a batch mode, either on a barge in a waterway or land based treatment center. While the invention has been described in reference to preferred illustrative embodiments, modifications of the preferred embodiments will be apparent to one skilled in the art upon reference to the specification. These modifications are intended to be within the scope of the invention.

I claim:

1. A method for treating dredged material comprising:

(a) removing bulk particles from the dredged material,

(b) adding liquid to the dredged material, and

(c) separating liquid from the dredged material thereby obtaining filtrate and a solid portion,

wherein contaminants are removed from the dredged material by subjecting the dredged material to at least one oxidation process.

2. A method according to claim 1 wherein the at least one oxidation process comprises admixing at least one oxidizing agent with the dredged material in step (b).

3. A method according to claim 1 wherein the at least one oxidation process comprises admixing at least one oxidizing agent with the solid portion.

4. A method according to claim 1 wherein the at least one oxidation process comprises admixing at least one oxidizing agent with the dredged material in step (b) and admixing at least one oxidizing agent with the solid portion

5. A method according to claim 1 comprising admixing at least one flocculating agent with the dredged material in step (b).

6. A method according to claim 2 wherein the at least one oxidizing agent is selected from the group consisting of oxygen, hydrogen peroxide, ozone, chlorine, chlorine dioxide, sodium hypochlorate, calcium hypochlorate, sodium chlorate, sodium chlorite, bleach, potassium permanganate and mixtures thereof.

7. A method according to claim 3 wherein the at least one oxidizing agent is selected from the group consisting of oxygen, hydrogen peroxide, ozone, chlorine, chlorine dioxide, sodium hypochlorate, calcium hypochlorate, sodium chlorate, sodium chlorite, bleach, potassium permanganate and mixtures thereof

8. A method according to claim 4 wherein the at least one oxidizing agent is selected from the group consisting of oxygen, hydrogen peroxide, ozone, chlorine, chlorine dioxide, sodium hypochlorate, calcium hypochlorate, sodium chlorate, sodium chlorite, bleach, potassium permanganate and mixtures thereof

9. A method according to claim 3 wherein the flocculating agent is a polyelectrolyte.

10. A method according to claim 1 further comprising forming a structural article from the solid portion.

* * * * *

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US005685900A

United States Patent [19]

Yuan et al.

[11] Patent Number: 5,685,900

[45] Date of Patent: Nov. 11, 1997

[54] **METHOD FOR BENEFICIATING DISCOLORED KAOLIN TO PRODUCE HIGH BRIGHTNESS COATING CLAY**

[75] Inventors: **Jun Yuan**, Milledgeville; **Ben E. Everett**, Tennile; **Windell R. Andrews**, Sandersville, all of Ga.

[73] Assignee: **ECC International Inc.**, Roswell, Ga.

[21] Appl. No.: **546,398**

[22] Filed: **Oct. 18, 1995**

[51] **Int. Cl.**[6] **B03D 3/06**; C04B 33/04; C04B 33/10

[52] **U.S. Cl.** **106/487**; 106/488; 501/148; 252/187.26; 252/186.21; 209/5; 209/10; 209/39; 423/118.1

[58] **Field of Search** 106/486, 487, 106/488; 252/186.21, 187.26; 209/5, 10, 39; 501/146, 148; 423/118.1

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Primary Examiner—Michael Marcheschi
Attorney, Agent, or Firm—Suzanne Kikel

[57] **ABSTRACT**

A method for beneficiating a low brightness fine particle size discolored kaolin crude to produce a high brightness coating clay. By combining the two beneficiating techniques of selective flocculation and ozonation, a synergistic phenomena occurs and a clay product of superior brightness and whiteness can be obtained from fine discolored clays that cannot be achieved by beneficiation with either process singularly. By passing the flocced clay through ozonation, the flocculant polymer left in the clay can be completely destroyed.

16 Claims, No Drawings

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METHOD FOR BENEFICIATING DISCOLORED KAOLIN TO PRODUCE HIGH BRIGHTNESS COATING CLAY

BACKGROUND OF THE INVENTION

This invention relates to the beneficiation of kaolin clays and clay minerals and, more particularly, is concerned with a method of removing a substantial portion of the titanium minerals and organics contained as impurities in fine particle size kaolin clays to produce a clay, suitable for coating paper, having markedly greater brightness and whiter color.

Kaolin clay coating pigments having very fine particle size and high brightness characteristics are widely utilized in the coating of merchant grade papers and various types of paperboard, wherein high gloss and smoothness of coating are required. Typically, these pigments are applied as a high solids aqueous suspension, i.e., a suspension including from approximately 60 to 75% by weight of clay solids. The size distribution of prior art pigments used for such purposes are usually such that of the order of 90 to 100% by weight thereof are of less than 2 micrometers equivalent spherical diameter (E.S.D.). Typically, further, the brightness characteristics (as measured by the standard specification established by Tappi procedure T-646 OS-75, are of the order of at least 90 on the so called G.E. scale. Among the further qualities of high solids coating clay slurries which are of paramount importance for achieving high quality coatings, are the viscosity characteristics of same. It may be noted in this connection that the term "viscosity", as used herein with respect to clay slurries, refers to such characteristics as determined by the procedures of Tappi method T 648su-72, as revised in 1972. This method sets forth specific procedures for determination of both the "low shear" and "high shear" viscosity. The latter, i.e. the high shear viscosity is considered of special importance in evaluating a high solids clay slurry for the aforementioned coating purposes.

Certain coating kaolins of the aforementioned type are particularly sought after for use in coating premium papers and paperboard. A product of this type is the ALPHAFINE® product of the present assignee, ECC International, Inc. This product is a high brightness, very fine particle size glossing clay, especially developed to meet the demands of the premium coated paper and paperboard producers. Such product provides the important combination of high sheet gloss and superior print quality required by these paper grades. The product can be effectively formulated into both air-knife and blade coating colors to achieve maximum board gloss. Typical physical properties of a product of the ALPHAFINE® type include a G.E. brightness of 90.5 and a particle size distribution such that at least 86% by weight of the particles have an E.S.D. of less than 0.5 micrometers. At a slurry solids content of 70%, the slurry will exhibit a Brookfield viscosity of about 300 cps at 20 rpm.

In a typical procedure for preparing a prior art premium coating day of the ALPHAFINE® type, a crude kaolin including cream Georgia kaolins in possible combination with grey crudes, is blunged and dispersed at high solids; degritted, and then scalped, diluted to 35–70% solids and classified to yield a fraction at about 90% less than 0.5 micrometers. This fraction is typically then subjected to oxidative bleaching, as with ozone, in order to bleach organic discolorants as may be present. The slurry is then subjected to a high intensity magnetic separation, and the recovered beneficiated clay is then, as is conventional, flocced and bleached with a reductive bleaching agent. The recovered material is filtered and then dispersed and dried as, for example, in a spray dryer or evaporator to yield the final output product.

However, natural occurring kaolin clays vary considerably in their color properties, even when produced from mines in the same locality or even from different sites in the same mine. The color of clays is largely due to discoloring contaminants, for example, titanium and iron minerals, organic and inorganic carbon, and impurity clay minerals such as smectite and illite-smectite mixed-layered clay mineral. Titanium and iron minerals and iron in the crystal structure of kaolinite and impurity clay minerals are largely responsible for the yellow brown shade. Organic and inorganic carbon is the main cause of the gray tint. Most of the natural occurring clays are discolored to a degree where no process available to the art could sufficiently improve their brightness and whiteness values to a level that would make them acceptable as a usable pigment or filter, particularly in the paper industry, even though some of them are within desired limits in other physical properties such as the viscosity of clay-water slurries and particle size distribution.

Many techniques have been developed in the recent years for removing impurities to improve clay products brightness. Among them are those which involve selective mining, magnetic separation, flotation, ozone oxidation, selective flocculation, and leaching. However, even with the many techniques for beneficiating clays which have been advanced over the years, there remains a very substantial portion of the clays available for mining which are not sufficiently beneficiated by such processes to achieve products of acceptable quality to the paper industry. This is particularly true with respect to so called "hard kaolins" from seconday kaolin clay deposits found in the Southeast, particularly in central and eastern Georgia.

Hard grey kaolin clays are well recognized in the kaolin art as having attributes which lend them to certain processing to yield very valuable products. These type of discolored kaolins are, for example, especially used to produce calcined filler pigments of high quality. Extensive discussions of hard grey kaolins may be found in McConnell, et al., U.S. Pat. No. 4,381,948 and in Fanselow, et al., U.S. Pat. No. 3,586, 523. The said clays are noteworthy for having a very fine particle size, but also are found in general to include high quantities of discoloring contaminants, including ferruginous impurities, and titaniferous impurities, i.e. titanium dioxide, which, in the iron-stained form in which it is present, produces discoloration in the said clays. Additionally, such clays in part derive their discoloration from sizable quantities of organic discolorants in addition to other common impurities. Certain aspects of the morphology of these clays would suggest that they might be useful for preparing very high quality coating clays as, for example, of the ALPHAFINE® type. However, previous efforts to do so have not been successful in yielding a product having both the desired brightness characteristics, as well as the low viscosity characteristics which are essential in such a high quality coating clay.

Previously, a process called "selective flocculation" has been used to try to upgrade Georgia "hard kaolin" to high brightness coating clay. Two fundamentally different approaches are known for clay beneficiation by selective flocculation: (1) The impurities are flocculated and the clay product is left in suspension; (2) the clay is flocculated and the impurities are left in supernatant suspension.

The first approach is less economical and therefore less desirable because a low recovery rate results from the simultaneous settlement of both clay and impurities and

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because of ineffectiveness with gray clays. Examples of this first approach disclosed in U.S. Pat. Nos. 3,701,417, 3,857,781, and 4,604,369.

The second approach is more desirable as a clay beneficiation process. Because clay particles are naturally charged on their surfaces, it is much easier and more effective to flocculate the clay particles rather than the impurity titanium minerals. The flocculated clay is also higher in solids concentration, which is more advantageous than the first approach where the clay product suspension is diluted after selective flocculation. Examples of this second approach are presented in U.S. Pat. Nos. 3,477,809 3,808,021, 3,837,482, 4,227,920, and U.K. Pat. No. 2,059,811. However, this second approach has been until now impractical, due primarily to the resultant contamination of the clay product by the presence of the flocculating reagent, which lowers the product brightness and is significantly deleterious to the product theology.

Pursuant to the foregoing, it may be regarded as an object of the present invention, to provide a novel, practical, and effective process for removing the discolored titanium and organic impurities in low brightness, fine particle size discolored kaolin crude to produce a high brightness and whiteness coating clay which displays excellent viscosity for paper coating applications and which contains a minimum amount of undesirable residual chemicals.

A further object of the invention, is to provide a process of the foregoing character which is especially useful in processing a crude which comprises a hard grey kaolin.

SUMMARY OF THE INVENTION

Now, in accordance with the present invention, a method is disclosed for beneficiating a low brightness fine particle size discolored kaolin crude to produce a high brightness coating clay. Unexpectedly it has been found that by combining the two beneficiating techniques of selective flocculation and ozonation, a synergistic phenomena occurs and a clay product of superior brightness and whiteness can be obtained from fine discolored clays that cannot be achieved by beneficiation with either process singularly. By passing the flocced clay through ozonation, the flocculant polymer left in the clay can be completely destroyed. Pursuant to the invention, a dispersed aqueous slurry is prepared from a fine particle size discolored crude kaolin typically having a water-washed G.E. brightness in the range of 75 to 85, a contaminant titania content of from 0.5 to 3.0 weight percent, a contaminant iron content of from 0 to 2% expressed as Fe_2O_3, and a P.S.D. such that at least 85% by weight of the particles are of less than 2 micrometers E.S.D. The slurry is classified to recover a kaolin fraction wherein at least 90% by weight of the particles are of less than 0.5 μm E.S.D. This recovered fraction is subjected as a slurry to a first oxidative bleaching to partially bleach organic discolorants and to facilitate a subsequent step of selective flocculation of the clay. The slurry from the first oxidative bleaching step is then selectively flocculated utilizing a high molecular weight anionic polyacrylamide or a copolymer of a polyacrylate and a polyacrylamide, to form a supernatant phase which is highly concentrated with said contaminant titania, and a flocced clay phase which is relatively devoid of titania, but which includes the bulk of remaining discolorant organics. The floes are then treated in aqueous suspension with gaseous ozone to destroy the flocculent polymer, thereby restoring the kaolin to a dispersed phase while further oxidizing the remaining discoloring organics. The ozonized kaolin is recovered and further beneficiated to provide the high brightness coating clay.

The crude utilized in the invention may comprise partially or entirely a hard grey kaolin which includes from 0.03 to 0.15% discoloring organics. The ozonation treatment can be carried out using gas contact apparatus including conventional bubbling apparatus or the like. The treatment level is typically at a dosage of 1.5–6 pounds ozone per ton of kaolin.

The product resulting from practice of the invention will have a brightness of at least 91 and displays a Hercules viscosity of less than 18 dynes at 2200 rpm when prepared as a 70% solids coating slurry. The product pigment in other instances may have a brightness of at least 93.

In some instances in practice of the invention, further brightness improvements can be achieved by incorporating a high shear mixing step prior to selective flocculation. A rotor and stator device such as a COWLES® mixer is suitable for this purpose. The shearing step can be conducted between the first oxidative bleaching and the selective flocculation, and may immediately proceed the flocculation step.

Typically, the first oxidative bleaching step in the process is at least partially effected with sodium hypochlorite. The process of the invention can be carried out as a batch operation; or can be conducted continuously by use of a thickener apparatus so that the overflow is impurity supernatant, and the underflow is flocced clay. A high capacity unit such as the well-known ENVIRO-CLEAN® thickener can be used for these purposes. Other thickeners which may be so employed are discussed at pages 573ff of the "Encyclopedia of Chemical Technology".

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Pursuant to the invention, the crude kaolin serving as the feed can typically comprise a hard grey crude of the type aforementioned, although other discolored kaolins can also be used. The grey crude typically has a G.E. brightness in the range of from about 75 to 85 and includes contaminant titania from about 0.5 up to 3.0% by weight of kaolin. Contaminant iron is also present, ranging up to about 2% expressed as Fe_2O_3. The particle size distribution of the crude is such that at least 85% by weight of the particles are of less than 2 micrometers E.S.D. This crude is blunged and dispersed at about 70% solids (more generally it can be prepared as 30 to 70% solids). Sodium carbonate and sodium hexametaphosphate can be used as dispersing agents. The resultant slurry is degritted as, for example, by being passed through a 20 mesh to 80 mesh screen. The slurry is then scalped, diluted to 35 to 40% solids, and classified in centrifuges to produce a fraction at about 90% less than 0.5 micron. Typically, at least 90% by weight of the particles are of less then 0.5 micrometers. This slurry is then subjected to an initial oxidative bleaching step preferably using sodium hypochlorite. The dosage of the hypochlorite is in the range of 0.5 to 3 gallons per ton of dry clay. The bleached slurry is typically aged overnight, i.e. for about 12 hours to 24 hours.

The resulting slurry is thereupon diluted to about 5 to 25% solids, typically around 10 to 12% solids, and is then subjected to a selective flocculation treatment. The preferred selective flocculation reagents comprise a high molecular weight anionic polyacrylamide or a copolymer of a polyacrylate and polyacrylamide. A preferred flocculating agent is the CALGON™ R50 polymer which is a weakly anionic copolymer of polyacrylate and polyacrylamide, available from Calgon Corporation of Pittsburgh, Pa. Concentrations

of the flocculating polymer or copolymer will generally be in the range of 0.01% to 0.1%, (or 0.3 to 5 lbs/ton dry clay), with about 2 pounds per ton dry clay being typical. It may be noted here that the first oxidative bleaching step which proceeds selective flocculation not only bleaches sizable proportions of the organic discolorants, but has a synergistic effect in facilitating formation of the flocs during the subsequent selective flocculation.

As a result of the selective flocculation, a supernatant phase forms which is highly concentrated in the contaminant titania. This supernatant phase is separated, and discarded or otherwise used. The purified flocs or sediment are preferably passed at about 30% solids through a high shear pump which break up the flocs, whereupon they are subjected as an aqueous suspension to ozonation at a dosage level of 1.5–6 pounds, typically about 2 pounds per ton of kaolin of the ozone. The ozone is preferably applied as a stream of bubbles which can be passed upwardly through the slurry. This can be a batch process, but preferably is a continuous process in which the ozone bubbles pass counter current to a flow of the slurry in a pipe or other conduit, such as mixed and packed column.

The ozone acts not only to destroy substantial portions of the remaining discoloring organics, but of equal importance, acts to destroy by oxidation the flocculent, i.e. the polymer which has been previously added. In consequence, the clay in the slurry is now in a dispersed phase and may be readily subjected to further beneficiation depending upon the contaminants. The slurry at about 30% solids or other dilute condition is thus typically passed through a high intensity magnetic separator, using apparatus of the type described in U.S. Pat. No. 3,627,678. The beneficiated material emerging from the magnetic separation may then be subjected, as is known in the art, to conventional flocculation and reductive bleaching as, for example, by addition of sulfuric acid with sodium hydrosulfite and aluminum sulphate. The recovered and bleached material can then be dried, as by filtering on a rotary vacuum filter or the like, after which the material can be reslurried, dispersed, and then dried by spray drying or by an evaporator.

The resulting material is found to be an excellent coating kaolin pigment having a brightness of at least 91 and preferably of at least 93. It displays a Hercules viscosity of less than 18 dynes of 4400 rpm when prepared as a 70% solids coating slurry.

The invention is further illustrated by the following Example:

EXAMPLE 1

The starting crude for this Example was a fine hard grey kaolin from a mine near Wrens, Ga. This crude was processed by two methods. First, by the method described in the background of this invention as being used for producing conventional ALPHAFINE®; and second, by means of the process of the invention. The initial crude was characterized by having a brightness of 84.6, a TiO_2 content of 2.03% and an iron content of 0.87% expressed as Fe_2O_3. The conventionally processed material was found to have a brightness of 91.2, a titania content of 1.47%, and an iron content of 0.76%. The sample processed by the method of the invention was found to have a much higher brightness of 93.3, a much lower titania content of 0.47% and a virtually similar iron content of 0.77%. Thus, the process of the invention was found with the same material to produce an improvement in brightness of 2.1 points, which is extremely significant in the pertinent art.

The process of the invention is particularly significant in terms of maintaining the rheological properties of the starting material. Previous art of the similar-type selective flocculation process has always resulted in a product with poor theology due to the residual contaminating flocculent, or the process could yield a product with comparable theology, but is economically unfeasible. This advantage of the present invention is illustrated in Table A by a comparison between a conventionally processed product (processed as for conventional ALPHAFINE®—see Example 1) and a sample processed in accordance with the invention—see Example 1. It would be noted that viscosity of the product of the invention is only slightly higher at low shear rate, and not much different at high shear rate.

TABLE A

Rheology:	Brookfield cps @ 20 rpm	Hercules dynes @ 4400 rpm
Sample #1		
Conventionally Processed Product	460	4.8
Product of Invention	530	6.7
Sample #2		
Conventionally Processed Product	220	4.1
Product of Invention	340	3.8

Although the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the instant disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the invention. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended hereto.

What is claimed is:

1. A method for beneficiating a low brightness, fine particle size discolored kaolin crude to produce a high brightness coating clay having a brightness of a least 89, comprising the steps of:

preparing a dispersed aqueous slurry from a fine particle size discolored crude kaolin having a solids content, a water washed G.E. brightness in the range of 75 to 85, a contaminant titania content of from 0.5 to 3.0%, a contaminant iron content of from 0 to 2%, expressed as Fe_2O_3, and a P.S.D. such that at least 85% by weight of the particles are of less than 2 μm E.S.D.;

classifying said slurry to recover a kaolin fraction wherein at least 90% by weight of the particles are of less than 0.5 μm E.S.D.;

subjecting said recovered fraction as a slurry to a first oxidative bleaching to partially bleach organic discolorants, and to facilitate subsequent flocculation of the clay;

selectively flocculating the solids of the slurry from said first oxidative bleaching step with a high molecular weight anionic polyacrylamide or a copolymer of polyacrylate and polyacrylamide, to form a supernatant phase which is concentrated with said contaminant titania, and a flocced clay phase having a reduced titania content, but which includes the remaining discolorant organics;

treating the flocs in aqueous suspension with gaseous ozone to destroy the flocculent polymer thereby restor-

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ing the kaolin to a dispersed phase, while further oxidizing the discoloring organics; and

recovering and further beneficiating the ozonized kaolin to provide said high brightness coating clay.

2. A method in accordance with claim 1, wherein said crude comprises a hard grey kaolin which includes from 0.03 to 0.15% discoloring organics.

3. A method in accordance with claim 1, wherein the said flocs in aqueous suspension are treated with said ozone in an amount of at least 1.5–6 lbs/ton of kaolin.

4. A method in accordance with claim 2, wherein said solids content is from 30 to 70 weight %.

5. A method in accordance with claim 4, wherein said slurry is classified at about 35 to 40% solids, and the recovered fraction is subjected to said first oxidative bleaching at about 30 to 35% solids.

6. A method in accordance with claim 1, wherein said first oxidative bleaching step is accomplished with sodium hypochlorite.

7. A method in accordance with claim 1, wherein said bleached slurry is subjected to selective flocculation at about 5 to 25% solids.

8. A method in accordance with claim 7, wherein said bleached slurry is subjected to selective flocculation at about 10 to 12% solids.

9. A method in accordance with claim 1, wherein said ozonized kaolin is further beneficiated by being subjected in aqueous suspension to intense magnetic separation.

10. A method in accordance with claim 9, wherein said kaolin clay is recovered from said magnetic separation, reductive bleached to remove ferruginous impurities, and is then filtered and dried.

11. A method in accordance with claim 1, wherein said coating clay has a brightness of at least 91, and displays a Hercules viscosity of less than 18 dynes at 4400 r.p.m. when prepared as a 70% solids coating slurry.

12. A method in accordance with claim 11, wherein said coating clay has a brightness of at least 93.

13. A method in accordance with claim 1, which is carried out as a continuous process.

14. A method in accordance with claim 1, which is carried out as a batch process.

15. A method in accordance with claim 1, which is carried out with an additional step of high shear mixing before selective flocculation.

16. A method in accordance with claim 1, wherein following said first oxidative bleaching, the slurry is aged prior to selective flocculation.

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(54) Title: ENZYME-ASSISTED CLARIFICATION AND DEWATERING OF WASTEWATER

(57) Abstract: A method of clarifying and dewatering wastewater comprising adding an effective clarifying and dewatering amount of one or more cellulolytic enzymes and one or more flocculants to the sludge to form a mixture of water and coagulated and flocculated solids and separating the coagulated and flocculated solids from the water.

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ENZYME-ASSISTED CLARIFICATION AND DEWATERING OF WASTEWATER

TECHNICAL FIELD

This invention concerns the use of cellulolytic enzyme preparations in combination with one or more flocculants to aid in clarifying and dewatering municipal and industrial wastewater.

BACKGROUND OF THE INVENTION

The dewatering and clarification of municipal and industrial sludges containing suspended organic solids is typically accomplished by mixing the sludge with one or more chemical reagents in order to induce a state of coagulation or flocculation of the solids which are then separated from the water using mechanical devices such as plate and frame filter presses, belt-filter presses, centrifuges, and the like.

For example, in a typical municipal sewage plant, wastewater remaining after coarse solids are settled out of the incoming sewage influent is conveyed into a biological clarifying stage, where the dissolved and suspended organic material is decomposed by microorganisms in the presence or absence of air. These processes are referred to as aerobic digestion and anaerobic digestion, respectively.

The organic matter obtained as a result of this decomposition is largely bound in the form of a mass of microorganisms. This mass is precipitated as an activated sludge. The water may be released into waterways or allowed to seep away in sewage irrigation fields, but the activated sludge must be dewatered prior to disposal.

Moreover, variations often occur in wastewater from any one source, leading to a variety of particle types which must be removed. For example, municipal sludge consists of primary and waste-activated sludges. The sludges typically contain a considerable amount of cellulose, arising from paper, rags and vegetable fibers. Cellulose accounts for 60 to 80 percent of the total carbohydrate and 15 to 25 percent of the total organic particulate. Municipal sludges generally contain a large proportion of sanitary wastewater from one or more residential communities. The influent is generally of a more biological nature in municipal sludges.

Industrial sludges, on the other hand, come from a variety of industries including paper, refinery, chemical, steel, aluminum and others. Primary solids vary considerably from industry to industry. In some industrial sludge from the refinery and chemical industries, very low amounts of primary solids are present. Most of the solids are from the waste-activated sludge process. The influent to an industrial wastewater plant is mainly process effluents, and it usually contains a lot of organic material. Steel and aluminum industrial sludge may contain steel and aluminum and some oils, whereas paper mill influent contains a very large proportion of fibers and solids from the process. The composition of industrial sludge is very different than that of municipal sludge and is quite specific to the industry. The nature of solids and content of solids can also vary greatly depending on the type of industries. The organics loading is generally higher in industrial influent than in municipal influent.

More particularly, in refineries, the primary wastewater treatment facilities remove most of the insoluble oils that come from the process units upstream of the wastewater treatment plant (WWTP). The contaminants are components of crude oils: paraffins, asphaltenes, aromatic hydrocarbons (including benzene, toluene, xylenes, etc.), aliphatic hydrocarbons, hydrogen sulfides, cyanate salts, ammonia, soaps and detergents, and methanol from deep offshore oilfields. The secondary or biological treatment facility must remove the water-soluble contaminants from the above list.

In the Chemical Processing Industry (CPI), the organics sent to the WWTP are more refined and thus more water-soluble and difficult to remove at the primary WWTP. The hydrocarbons are more refined and functionalized, e.g. manufactured amines, esters, ethers, carboxylic acids, lactones, lactams, etc. These functionalized hydrocarbons are more water-soluble, and thus the biological treatment program is under duress and stress to remove the contaminants prior to discharge.

For the steel and aluminum industries, the hydrocarbons going to the wastewater treatment plant consist of highly functionalized materials. Heavy greases and lubricants are used as well as greater amounts of surfactants designed to create oil-in-water emulsions. Furthermore, metal solids from the process, such as iron oxides and aluminum oxides, are present in higher quantities and help stabilize oil contamination in water.

The objective of clarification and dewatering processes is to maximize the efficiency of water removal, as decreasing the amount of water retained in the dewatered solids leads to decreased transport and disposal costs. Therefore, there is an ongoing need for improved clarification and dewatering technologies that are suitable for use across the spectrum of wastewaters.

Dewatering of biologically clarified sludges using a hydrolytic enzyme preparation containing cellulases followed by a high molecular weight cationic flocculant is disclosed in European Patent No. 291 665.

Dewatering of sludges using cellulolytic enzyme preparations in combination with enzymatic or chemical oxidants followed by a high molecular weight flocculant is disclosed in commonly-owned U.S. Patent Application Serial Nos. 10/059,473 and 10/347,891, now U.S. Patent Nos. 6,733,673 and 6,733,674, respectively.

SUMMARY OF THE INVENTION

This invention is a method of clarifying and dewatering industrial wastewater comprising sequentially

i) adding an effective amount of one or more cellulolytic enzymes to the wastewater;

ii) adding an effective amount of one or more flocculants to the wastewater to form a mixture of water and coagulated and flocculated solids; and

iii) separating the coagulated and flocculated solids from the water.

Benefits of using enzymes as described herein in wastewater treatment include polymer dosage reduction, cake dryness improvement, improved settling of sludge, better filtrate quality from the dewatering operation and faster wastewater clarification.

DETAILED DESCRIPTION OF THE INVENTION

Cellulolytic enzymes refers to a class of enzymes involved in hydrolyzing cellulose and other water-soluble cyclodextrins. The enzymes are found in natural processes via biological operations or are synthesized by a variety of microorganisms

including fungi, actinomycetes, myxobacteria and true bacteria and also by plants. The specific enzymes can also be engineered by a specific type of biological operation or by purification.

The cellulolytic enzyme preparations used in the practice of this invention are commercially available enzymes obtained from microorganism cultures. The preparations may contain a single cellulolytic enzyme or mixture of cellulolytic enzymes. Additional hydrolytic enzymes including proteases, glycoproteinases, lipases, alpha-amylases, β-glucanases, hemicellulases, laminarinases, and the like may also be present as impurities in the enzyme preparation.

Cellulolytic enzymes useful in the practice of this invention include one or more cellulases present in the enzyme system that hydrolyzes cellulose to glucose including cellobiohydrolase (1,4-β-D-glucan cellobiohydrolase, EC 3.2.1.91), including endo-1,4-β-glucanase (endo-1,4-β-D-glucan 4-glucanohydrolase, EC 3.2.1.4), exo-1,4-β-glucanase and β-glucosidase (EC 3.2.1.21).

In a preferred aspect of this invention, the cellulolytic enzyme is a mixture of endo-1,4-β-glucanase, exo-1,4-β-glucanase and 1,4-β-glucosidase.

In another preferred aspect, the cellulolytic enzyme is a mono-component enzyme preparation having only endoglucanase activity.

In another preferred aspect, the mono-component enzyme preparation comprises endo-1,4-β-glucanase.

Enzyme preparations having only endoglucanase activity useful in the practice of this invention are described in U.S. Patent Nos. 6,001,639 and 6,387,690, incorporated herein by reference.

The cellulolytic enzyme preparations are generally available as solutions in water, which can be further diluted. In the process of this invention, aqueous solutions having an enzyme concentration of from about 0.01 to about 100 grams of enzyme protein per liter are typically used.

In a preferred aspect of this invention, the wastewater is an industrial sludge.

In another preferred aspect, the industrial sludge is an activated sludge.

A particular type of sludge is an autothermal (or autoheated) thermophilic aerobic digestion (ATAD) sludge. ATAD refers to an aerobic sludge digestion process

that operates in the thermophilic temperature range (about 40 °C to about 80 °C) with supplemental heat. The ATAD process may be used on both industrial and municipal sludges.

The thermophilic bacteria that flourish at the elevated temperatures used in the ATAD process have a much higher rate of metabolism, which results in a much faster rate of volatile solids destruction compared to anaerobic digestion operating in the mesophilic range, or conventional aerobic digestion operating near ambient wastewater temperatures. Adequate volatile solids destruction (about 35-45 percent) is achieved in an ATAD system in about 6-8 days, compared to about 30-60 days in an anaerobic digester or about 20-60 days in an aerobic digester. Additionally, the elevated temperatures in an ATAD system are effective in destroying pathogens, with pathogen reduction to non-detectable levels being achieved within about five hours at temperatures of 50 °C or better. Thus, ATAD requires not only less tankage but will produce a Class A sludge, whereas conventional aerobic and anaerobic digestion will produce only Class B sludge due to the pathogen content in municipal sludges.

ATAD sludge, however, is difficult to dewater. Experience from full-scale operations show that ATAD results in deterioration of biosolids dewatering properties, and increased costs of biosolids conditioning. ATAD also results in smaller and finer biosolids flocs that may contribute to the deteriorated dewaterability and increased demands of conditioning polymers.

Furthermore, thermophilic bacteria produce various biopolymers such as polysaccharides, starch, proteins and lipoglycoproteins. These materials can soak up water like a sponge and inhibit the release of the water. Chemical treatment involves using high molecular weight cationic polymers and the use of various dewatering equipment including belt presses, centrifuges, screw presses, plate and frame filter presses and gravity belt thickeners. In most cases, either chemical or equipment processes cannot completely force the water from the biopolymers. Thus the percent solids are typically lower for ATAD sludges. We have discovered that enhanced dewatering of ATAD sludges can be attained by using cellulolytic enzymes in combination with polymeric flocculants.

Accordingly, in another preferred embodiment, the sludge is an autothermal thermophilic aerobic digestion sludge.

We have also discovered treating of municipal or industrial wastewater with a mono-component enzyme preparation having only endoglucanase activity confers additional benefits over treatment with a multi-component cellulolytic enzyme preparation, particularly a reduction in BOD (biological oxygen demand) of the resulting sludge over sludge that results from treatment of the wastewater with multi-component enzyme.

Accordingly, in another preferred aspect, this invention is a method of clarifying wastewater comprising sequentially

i) adding an effective amount of a mono-component enzyme preparation having only endoglucanase activity to the wastewater;

ii) adding an effective amount of one or more flocculants to the wastewater to form a mixture of water and coagulated and flocculated solids; and

iii) separating the coagulated and flocculated solids from the water.

In another preferred aspect, the wastewater is selected from the group consisting of municipal sludge and industrial sludge.

In a preferred aspect, the sludge is an activated sludge.

In another preferred aspect, the mono-component enzyme preparation comprises endo-1,4-β-glucanase.

In another preferred aspect, the sludge is an autothermal thermophilic aerobic digestion sludge.

In a typical application, about 0.125 to about 5 L/dry ton, preferably about 0.125 to about 1 L/dry ton of the enzyme preparation is added under well mixed conditions to the wastewater. The enzyme treatment is carried out at ambient process water temperature without further temperature adjustment, noting however, that the process water temperatures are typically higher than ambient temperature, often as warm as 60 °C. As noted above, ATAD processes can operate at a temperature up to about 80 °C. Mixing is continued for several minutes to several days, preferably about 30 minutes to about 6 days, after which time the flocculants and any coagulants are

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added. The wastewater is then mechanically dewatered, for example by devices such as plate and frame filter presses, belt-filter presses, centrifuges, and the like.

Suitable flocculants for use in this invention generally have molecular weights in excess of 1,000,000 and often 20,000,000. The polymeric flocculant is typically prepared by vinyl addition polymerization of one or more cationic monomers, by copolymerization of one or more cationic monomers with one or more nonionic monomers, by polymerization of one or more cationic monomers with one or more anionic monomers and optionally one or more nonionic monomers to produce an amphoteric polymer, by polymerization of one or more anionic monomers or by copolymerization of one or more anionic monomers with one or more nonionic monomers.

While cationic polymers may be formed as cationic polymers, it is also possible to react certain non-ionic vinyl addition polymers to produce cationically charged polymers. Polymers of this type include those prepared through the reaction of polyacrylamide with dimethylamine and formaldehyde to produce a mannich derivative.

The flocculant may be used in the solid form, as an aqueous solution, as a water-in-oil emulsion, or as a dispersion in water. Representative cationic polymers include copolymers and terpolymers of (meth)acrylamide with dimethylaminoethyl methacrylate (DMAEM), dimethylaminoethyl acrylate (DMAEA), diethylaminoethyl acrylate (DEAEA), diethylaminoethyl methacrylate (DEAEM) or their quaternary ammonium forms made with dimethyl sulfate, methyl chloride or benzyl chloride. A preferred cationic flocculant is dimethylaminoethylacrylate methyl chloride quaternary salt/acrylamide copolymer.

Representative anionic polymers include homopolymers of (meth)acrylic acid and its salts and copolymers of (meth)acrylic acid and salts thereof with (meth)acrylamide. A preferred anionic flocculant is acrylic acid/acrylamide copolymer.

The dose of flocculant depends on the properties of the sludge being treated and can be empirically determined by one of skill in the art. In general, the flocculant

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polymer dose is from about 50 ppm to about 5000 ppm, preferably from about 100 to about 1000 ppm, based on polymer solids, per dry ton solids.

In another preferred aspect, one or more coagulants are added to the wastewater after the enzyme treatment.

Water-soluble coagulants are well known, and commercially available. Suitable coagulants include polymeric coagulants and inorganic coagulants such as aluminum chloride, ferric chloride, ferric sulfate, and the like. Inorganic coagulants are preferred for dewatering of ATAD sludges.

Many water-soluble polymeric coagulants are formed by condensation polymerization. Examples of polymers of this type include epichlorohydrin-dimethylamine, and epichlorohydrin-dimethylamine-ammonia polymers.

Additional polymeric coagulants include polymers of ethylene dichloride and ammonia, or ethylene dichloride and dimethylamine, with or without the addition of ammonia, condensation polymers of multifunctional amines such as diethylenetriamine, tetraethylenepentamine, hexamethylenediamine and the like with ethylenedichloride and polymers made by condensation reactions such as melamine formaldehyde resins.

Additional polymeric coagulants include cationically charged vinyl addition polymers such as polymers and copolymers of diallyldimethylammonium chloride, dimethylaminoethylmethacrylate, dimethylaminomethylmethacrylate methyl chloride quaternary salt, methacrylamidopropyltrimethylammonium chloride, (methacryloxyloxyethyl)trimethyl ammonium chloride; diallylmethyl(β-propionamido)ammonium chloride; (β-methacryloxyloxyethyl)trimethyl-ammonium methylsulfate; quaternized polyvinyllactam; dimethylamino-ethylacrylate and its quaternary ammonium salts; and acrylamide or methacrylamide which has been reacted to produce the mannich or quaternary mannich derivative. The molecular weights of these cationic polymers, both vinyl addition and condensation, range from as low as several hundred to as high as one million. Preferably, the molecular weight range should be from about 20,000 to about 1,000,000.

The foregoing may be better understood by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the invention.

Example 1

Dewatering of a chemical industry sludge with a mono-component enzyme preparation having only endoglucanase activity.

A sample of mixed sludge from a large, midwestern chemical plant is obtained. The sludge is from a thickener and is taken prior to dewatering. The sludge has a suspended solids concentration of 6.5%. The sludge mixture consists of 60% secondary and 40% primary sludge. Two beakers containing 2000 grams of sludge are prepared. In one beaker, the sludge sample is mixed with 0.5 L of mono-component cellulolytic enzyme (endo-1,4-β-glucanase, EC 3.2.1.4, optimum pH range 5.5-7.5, available from Novozymes A/S, Bagsvaerd, Denmark under the designation NS-51008) per dry ton of sludge solids. In the second beaker, an equivalent amount of demineralized water is added to equalize the volume. The two beakers are maintained at 32 °C using a water bath and the contents are well mixed by a mechanical mixer stirring at 100 RPM. At the end of 48 hours, each sample is conditioned with a cationic polymer solution (40 mole percent dimethylaminoethylacrylate methyl chloride quaternary salt/acrylamide latex copolymer, RSV 12-19, available from Nalco Company, Naperville, IL) at several dosages. The conditioned samples are drained using filter media, and the rate of filtration is measured as a function of time. This test is commonly used to evaluate the effect of additives on the rate of filtration. The results are shown in Table 1. As can be seen, the rate of filtration is significantly better in the sample with the mono-component cellulolytic enzyme added compared to the control sample, especially at 250 and 275 ppm of cationic polymer.

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Table 1

Effect of a mono-component cellulolytic enzyme on drainage

Volume (mL)	Cationic Polymer (ppm)	10 sec control (ml)	10sec Mono Component Enzyme (ml)
8	200	32.7	36.0
10	250	39.7	66.1
11	275	48.7	56.4
12	300	63.5	68.0

Example 2

Dewatering of a chemical industry sludge with a multi-component cellulolytic enzyme preparation.

A sample of mixed sludge from a large southern petrochemical plant is obtained. The sludge is a blend of 1:1 digester influent and effluent. The sludge has a suspended solids concentration of 3.5%. The sludge mixture consists of 70% secondary and 30% primary sludge. Two containers, each holding 5000 grams of sludge, are prepared. In one container, the sludge sample is mixed with 0.5 L per dry ton of multi-component cellulolytic enzyme preparation containing cellulases, hemicellulases, xylanases (EC 3.2.1.8) and pentosanases (SP-342, available from Novozymes A/S, Bagsvaerd, Denmark). In the second container, an equivalent amount of demineralized water is added to equalize the volume. The two containers are maintained at 32 °C using a heater and the contents are well mixed with a mechanical mixer stirring at 100 RPM. The contents are kept under anaerobic conditions. At the end of five days, each sample is conditioned with a cationic polymer solution (50 mole percent dimethylaminoethylacrylate methyl chloride quaternary salt/acrylamide latex copolymer, RSV 8-12, available from Nalco Company, Naperville, IL) at several dosages. The conditioned samples are drained using a filter media, and the rate of filtration is measured as a function of time. This test is commonly used to evaluate the effect of additives on the rate of filtration. The results are shown in Table 2. As can be seen, the rate of filtration is significantly better

in the sample with the multi-component cellulolytic enzyme added compared to the control.

Table 2
Effect of a multi-component cellulolytic enzyme on drainage

Sludge	Cationic Polymer Solution (ml)	Cationic Polymer (ppm)	5 sec (ml)	10 sec (ml)	15 sec (ml)	30 sec (ml)	60 sec (ml)
Control	12	300	34	40	44	50	70
Control	13	325	46	56	66	80	104
Multi Component	12	300	46	54	66	78	94
Multi Component	13	325	54	66	74	88	102

Example 3

Dewatering of ATAD sludge with a mono-component enzyme preparation having only endoglucanase activity.

The enzyme treatment is conducted on a 1:3 blend of sludge from the gravity belt thickener (GBT) and autothermal thermophilic aerobic digestion (ATAD) holding tank from a southern CPI plant. The sample is divided, and each 4-L portion is placed into a 5-L, four-necked, round-bottom flask fitted with an overhead stirrer, thermometer probe, air inlet and condenser. For each flask, air is introduced via the air inlet, and the sample is agitated to ensure thorough mixing and heated to140 °F. The sludge has a solids concentration of 3.64% and consists of 25% GBT sludge and 75% ATAD sludge. To one of the flasks marked "Treated" is added 0.5 L per dry ton of mono-component cellulolytic enzyme (endo-1,4-β-glucanase, EC 3.2.1.4, optimum pH range 5.5-7.5, available from Novozymes A/S, Bagsvaerd, Denmark, under the designation NS-51008). In the second beaker, an equivalent amount of demineralized water is added to equalize the volume. The experiment lasts 14 days to duplicate the retention time of the ATAD system.

At the end of 14 days, the sludge is dewatered using ferric sulfate at various dosages and anionic flocculant (50 mole percent anionic charge dry polymer, 90%

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actives, available from Nalco Company, Naperville, IL) at 100 ppm. Free drainage is recorded at 5, 10, 15 and 30 seconds, and the 10-second data is graphed (see Table 3). The data is shown below. Using the enzyme material, more free water is released at lower dosages of ferric sulfate, significantly reducing the coagulant dosage by at least 75%.

Table 3

Effect of mono-component enzyme on free drainage of ATAD sludge.

	Dosage of Ferric Sulfate, ppm (free drainage recorded at 10 seconds)				
	2000	4000	6000	8000	10000
Treated	110 mL	125 mL	120 mL	110 mL	80 mL
Untreated		30 mL	80 mL	90 mL	105 mL

Example 4

Dewatering of municipal sludge with a mono-component enzyme preparation having only endoglucanase activity.

A sample of mixed sludge from a large midwestern municipal plant is obtained. The sludge is from an anaerobic digester and is taken prior to dewatering. The sludge has a suspended solids concentration of 2.3%. Two plastic bottles containing 2000 grams of sludge are prepared. In one bottle, the sludge sample is mixed with 0.5 L per dry ton of mono-component cellulolytic enzyme (endo-1,4-β-glucanase, EC 3.2.1.4, optimum pH range 5.5-7.5, available from Novozymes A/S, Bagsvaerd, Denmark, under the designation NS-51008). In the second beaker, an equivalent amount of demineralized water is added to equalize the volume. The two bottles are mixed at 100 RPM and maintained at 32 °C using incubator shaker equipment. At the end of 120 hours, each sample is conditioned with a cationic polymer solution (50 mole percent dimethylaminoethylacrylate methyl chloride quaternary salt/acrylamide latex copolymer, RSV 18-23, available from Nalco Company, Naperville, IL) at several dosages. The conditioned samples are drained using filter media, and the rate of filtration is measured as a function of time. This test is commonly used to evaluate the effect of additives on the rate of filtration. The results are shown in Table 4. As can

be seen, the rate of filtration is significantly better in the sample with the mono-component cellulolytic enzyme added compared to the control sample.

Table 4

Effect of a mono-component cellulolytic enzyme on municipal sludge drainage

Volume (ml)	Cationic Polymer (ppm)	10 sec control (ml)	10 sec Mono-Component Enzyme (ml)
5	125	18.1	40.0
7	175	81.4	115.1
7.5	187.5	94.2	138.3
8	200	120.4	147.7

Example 5

Clarification of refinery wastewater using a mono-component enzyme preparation having only endoglucanase activity.

The enzyme treatment is conducted on a 2:1 blend of sludge from the aeration basin influent and secondary clarifier recycle from a refinery wastewater treatment system. The suspended solids concentration is 1.2%. The sample is divided and each 4-L portion is placed into a 5-L, four-necked, round bottom flask fitted with an overhead stirrer, thermometer probe, air inlet and condenser. For each flask, air is introduced via the air inlet, and the sample is agitated to ensure thorough mixing and heated to 30 °C. To one of the flasks marked "Treated" is added 0.5 L per dry ton of mono-component cellulolytic enzyme (endo-1,4-β-glucanase, EC 3.2.1.4, optimum pH range 5.5-7.5, available from Novozymes A/S, Bagsvaerd, Denmark, under the designation NS-51008). In the second beaker, an equivalent amount of demineralized water is added to equalize the volume. The experiment lasts 12 hours to duplicate the retention time of the aeration basin and secondary clarifier process.

At the end of 12 hours, 1-L of sludge from each reactor is placed in a 1-L graduated cylinder. Cationic polymer (10 ppm, 30 mole percent dimethylaminoethylacrylate methyl chloride quaternary salt/acrylamide latex

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copolymer, RSV 18-25, available from Nalco Company, Naperville, IL) is added and each cylinder is inverted six times to simulate the transfer of sludge from the aeration basin to the clarifier. The amount of free water (because of settling) is measured in milliliters (mL) at various times. As shown in Table 5, the enzyme-treated sludge settled more quickly and had less sludge volume than an untreated sample.

Table 5

Effect of mono-component cellulolytic enzyme on wastewater clarification.

	10 ppm cationic polymer			
	5 min	10 min	15 min	30 min
Treated	400	540	590	660
Untreated	30	80	130	330

	20 ppm cationic polymer			
	5 min	10 min	15 min	30 min
Treated	410	520	550	610
Untreated	100	240	310	410

	30 ppm cationic polymer			
	5 min	10 min	15 min	30 min
Treated	200	475	475	500
Untreated	100	200	220	280

Changes can be made in the composition, operation and arrangement of the method of the invention described herein without departing from the concept and scope of the invention as defined in the claims.

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CLAIMS

1. A method of clarifying and dewatering an industrial wastewater comprising sequentially

i) adding an effective amount of one or more cellulolytic enzymes to the wastewater;

ii) adding an effective amount of one or more flocculants to the wastewater to form a mixture of water and coagulated and flocculated solids; and

iii) separating the coagulated and flocculated solids from the water.

2. The method of claim 1 wherein wastewater is an industrial sludge.

3. The method of claim 2 wherein the industrial sludge is an activated sludge.

4. The method of claim 2 wherein the industrial sludge is an autothermal thermophilic aerobic digestion sludge.

5. The method of claim 1 wherein the cellulolytic enzymes comprise a mixture of endo-1,4-β-glucanase, exo-1,4-β-glucanase and 1,4-β-glucosidase.

6. The method of claim 1 wherein the cellulolytic enzyme is a mono-component enzyme preparation having only endoglucanase activity.

7. The method of claim 6 wherein the mono-component enzyme preparation comprises endo-1,4-β-glucanase.

8. The method of claim 4 wherein the cellulolytic enzyme is a mono-component enzyme preparation having only endoglucanase activity.

9. The method of claim 8 wherein the mono-component enzyme preparation comprises endo-1,4-β-glucanase.

10. The method of claim 2 wherein the cellulolytic enzyme is a mono-component enzyme preparation having only endoglucanase activity.

11. The method of claim 10 wherein the mono-component enzyme preparation comprises endo-1,4-β-glucanase.

12. The method of claim 1 further comprising adding one or more coagulants to the wastewater.

13. The method of claim 9 further comprising adding one or more coagulants to the wastewater.

14. A method of clarifying and dewatering wastewater comprising sequentially

i) adding an effective amount of a mono-component enzyme preparation having only endoglucanase activity to the wastewater;

ii) adding an effective amount of one or more flocculants to the wastewater to form a mixture of water and coagulated and flocculated solids; and

iii) separating the coagulated and flocculated solids from the water.

15. The method of claim 14 wherein the wastewater us selected from the group consisting of municipal sludge and industrial sludge.

16. The method of claim 15 wherein the sludge is an activated sludge.

17. The method of claim 14 wherein the mono-component enzyme preparation comprises endo-1,4-β-glucanase.

18. The method of claim 15 wherein the sludge is an autothermal thermophilic aerobic digestion sludge.

19. The method of claim 14 further comprising adding one or more coagulants to the wastewater.

20. The method of claim 18 further comprising adding one or more coagulants to the sludge.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US05/01576

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C02F 1/00
US CL : 210/606, 609, 631, 632, 721, 725, 727, 728, 734

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)
U.S. : 210/606, 609, 631, 632, 721, 725, 727, 728, 734

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0291665 A (ROHM) 02 January 1991, see entire doccument	1-4
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Y		5-11, 12, 14-20
Y	US 6,001,639 A (SCHULEIN et al) 14 December 1999, see entire document	5-11, 14-20
Y	US 5,827,432 A (HUHTAMAKI et al) 27 October 1998, see entire document	12, 19, 20
Y,P	US 6,733,673 B2 (SARKAR et al) 11 May 2004, see entire document	1-20
Y,P	US 6,733,674 B2 (SARKAR et al) 11 May 2004, see entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document 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 cited 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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 May 2005 (14.05.2005)	31 MAY 2005

Name and mailing address of the ISA/US	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	RICHARD CRISPINO Telephone No. 571-272-1700 DEBORAH A. THOMAS PARALEGAL SPECIALIST ~~GROUP 1300~~

Form PCT/ISA/210 (second sheet) (July 1998)

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PATENT COOPERATION TREATY

From the RECEIVING OFFICE

To:
CIBA SPECIALTY CHEMICALS PLC
Patents Department
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GRANDE BRETAGNE

PCT

NOTIFICATION OF THE INTERNATIONAL APPLICATION NUMBER AND OF THE INTERNATIONAL FILING DATE

(PCT Rule 20.5(c))

Date of mailing *(day/month/year)*	26-01-2007
Applicant's or agent's file reference: MP/3-22379	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2007/050084	04/01/2007	18/01/2006

Applicant: CIBA SPECIALTY CHEMICALS HOLDING INC.

Title of the invention:

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.
2. The applicant is further notified that the record copy of the international application was transmitted to the International Bureau on the above date of mailing.
3. ☐ Other: _____

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29 JAN 2007

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

Name and mailing address of the Receiving Office	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040 Fax: (+31-70) 340-3016	Di Miceli, Giuseppe

Form PCT/RO/105 (July 1992; reprint January 2004)

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PCT REQUEST

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0	**For receiving Office use only**	
0-1	International Application No.	**PCT/EP2007/050084**
0-2	International Filing Date	**04 JAN 2007 (04.01.2007)**
0-3	Name of receiving Office and "PCT International Application"	**RO/EP**

0-4	**Form PCT/RO/101 PCT Request**	
0-4-1	Prepared Using	PCT Online Filing Version 3.5.000.176 MT/FOP 20020701/0.20.4rc.2.7
0-5	**Petition** The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	**Receiving Office (specified by the applicant)**	European Patent Office (EPO) (RO/EP)
0-7	**Applicant's or agent's file reference**	MP/3-22379
I	**Title of invention**	CONCENTRATION OF SUSPENSIONS
II	**Applicant**	
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II-11	Applicant's registration No. with the Office	2199764.8

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III-1	**Applicant and/or inventor**	
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III-3-7	State of residence	GB

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III-4	**Applicant and/or inventor**	
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III-5	**Applicant and/or inventor**	
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III-5-5	Address	7 Blakehill Avenue Eccleshill Bradford West Yorkshire BD2 3JT United Kingdom
III-5-6	State of nationality	GB
III-5-7	State of residence	GB
IV-1	**Agent or common representative; or address for correspondence**	
	No agent or common representative is/ has been appointed; the following special address should be used as:	address for correspondence
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IV-1-2	Address	Patent Department PO Box 38 Cleckheaton Road Low Moor Bradford West Yorkshire BD12 0JZ United Kingdom
IV-1-3	Telephone No.	+44 1274 417446
IV-1-4	Facsimile No.	+44 1274 417406

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PCT REQUEST

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V	DESIGNATIONS		
V-1	**The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.**		
VI-1	**Priority claim of earlier national application**		
VI-1-1	Filing date	18 January 2006 (18.01.2006)	
VI-1-2	Number	0601000.3	
VI-1-3	Country	GB	
VII-1	**International Searching Authority Chosen**	European Patent Office (EPO) (ISA/EP)	
VIII	**Declarations**	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	–	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	–	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	–	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	–	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	–	
IX	**Check list**	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	5	✓
IX-2	Description	44	✓
IX-3	Claims	2	✓
IX-4	Abstract	1	✓
IX-5	Drawings	1	✓
IX-7	TOTAL	53	
	Accompanying Items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	–	✓
IX-17	PCT-SAFE physical media	–	–
IX-19	**Figure of the drawings which should accompany the abstract**		
IX-20	**Language of filing of the international application**	English	

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PCT REQUEST

Print Out (Original in Electronic Form)

X-1	**Signature of applicant, agent or common representative**	(PKCS7 Digital Signature)
X-1-1	Name	GB, Ciba Specialty Chemicals Water Treatment Ltd., C. Choppen 1487
X-1-2	Name of signatory	
X-1-3	Capacity	

FOR RECEIVING OFFICE USE ONLY

10-1	**Date of actual receipt of the purported international application**	**04 JAN 2007 (04.01.2007)**
10-2	**Drawings:**	X
10-2-1	Received	
10-2-2	Not received	
10-3	**Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application**	
10-4	**Date of timely receipt of the required corrections under PCT Article 11(2)**	
10-5	**International Searching Authority**	ISA/EP
10-6	**Transmittal of search copy delayed until search fee is paid**	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	**Date of receipt of the record copy by the International Bureau**	

199

PCT

From the INTERNATIONAL BUREAU

To:

CIBA SPECIALTY CHEMICALS HOLDING PLC
Patent Department
P.O. Box 38
Cleckheaton Road, Low Moor
Bradford, West Yorkshire BD2 3JT
ROYAUME-UNI

NOTIFICATION OF RECEIPT OF RECORD COPY

(PCT Rule 24.2(a))

Date of mailing *(day/month/year)*	IMPORTANT NOTIFICATION
22 February 2007 (22.02.2007)	
Applicant's or agent's file reference	International application No.
MP/3-22379	PCT/EP2007/050084

The applicant is hereby **notified** that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

CIBA SPECIALTY CHEMICALS HOLDING INC. (for all designated States except US)
MOODY, Gillian et al (for US)

International filing date: 04 January 2007 (04.01.2007)
Priority date(s) claimed: 18 January 2006 (18.01.2006)
Date of receipt of the record copy by the International Bureau: 29 January 2007 (29.01.2007)
List of designated Offices:

AP: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW
EA: AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
EP: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
OA: BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
National: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

ATTENTION: The applicant should carefully check the data appearing in this notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau. **In addition, the applicant's attention is drawn to the information contained in the Annex**, relating to:

- time limits for entry into the national phase - **see updated important information (as of April 2002)**
- requirements regarding priority documents (if applicable)

A copy of this notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer
Saadallah Soumia
Facsimile No. +41 22 338 70 80
Telephone No. +41 22 338 84 21

International application No.
PCT/EP2007/050084

INFORMATION ON ENTERING THE NATIONAL PHASE

The applicant is reminded that the **"national phase" must be entered** before each of the designated Offices indicated on the cover sheet of this notification by paying national fees and furnishing translations, as prescribed by Articles 22 and 39 and the applicable national laws. In addition, the applicant may also have to comply with **other special requirements** applicable in certain Offices. It is the **applicant's responsibility** to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most Offices do not issue reminders to applicants in connection with the entry into the national phase.

The **applicable time limit** for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date, not only in respect of any elected Office if a demand for international preliminary examination is filed before the expiration of 19 months from the priority date (see Article 39(1)), but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see *PCT Gazette* No. 44/2001 of 1 November 2001, pages 19926, 19932 and 19934, as well as the *PCT Newsletter*, October and November 2001 and February 2002 issues.

In practice, **time limits other than the 30-month time limit will continue to apply, for various periods of time**, in respect of certain designated or elected Offices. For **regular updates on the applicable time limits (20, 21, 30 or 31 months, or other time limit)**, Office by Office, refer to the *PCT Gazette* ("Section IV" part published on a weekly basis), to the *PCT Newsletter* (on a monthly basis) and to the relevant National Chapters in Volume II of the *PCT Applicant's Guide* (the paper version of which is updated usually twice a year and the Internet version of which is updated usually on a weekly basis). Finally, a cumulative table of all applicable time limits for entering the national phase is available from WIPO's Internet site, via links from various pages of the site, including those of the *Gazette*, *Newsletter* and *Guide*, at http://www.wipo.int/pct/en/index.html.

Information about the requirements for **filing a demand for international preliminary examination** is set out in the *PCT Applicant's Guide*, Volume I/A, Chapter IX. Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 16 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before the date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 16-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 16-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau and if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances (Rule 17.1(c)).

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit (and all other PCT time limits) is the filing date of the earliest application whose priority is claimed (Article 2(xi)(b)).

PATENT COOPERATION TREATY

PCT/EP2007/050084

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

CIBA SPECIALTY CHEMICALS HOLDING PLC
Patent Department
P.O. Box 38
Cleckheaton Road, Low Moor
Bradford, West Yorkshire BD2 3JT
ROYAUME-UNI

Date of mailing *(day month year)* 23 February 2007 (23.02.2007)	
Applicant's or agent's file reference MP/3-22379	**IMPORTANT NOTIFICATION**
International application No. PCT/EP2007/050084	International filing date *(day month year)* 04 January 2007 (04.01.2007)
International publication date *(day month year)* **Not yet published**	Priority date *(day month year)* 18 January 2006 (18.01.2006)
Applicant CIBA SPECIALTY CHEMICALS HOLDING INC. et al	

1. By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).

2. *(If applicable)* The **letters "NR"** appearing in the right-hand column denote **a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau** under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

3. *(If applicable)***An asterisk (*)** appearing next to a date of receipt, in the right-hand column, denotes **a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b)** (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
18 January 2006 (18.01.2006)	0601000.3	GB	29 January 2007 (29.01.2007)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer

Yolaine Cussac

Facsimile No. +41 22 338 82 70
Telephone No. +41 22 338 90 12

WO 2007/082797
PCT/EP2007/050084

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

FIRST NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION (TO DESIGNATED OFFICES WHICH DO NOT APPLY THE 30 MONTH TIME LIMIT UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:

CIBA SPECIALTY CHEMICALS HOLDING PLC
Patent Department
P.O. Box 38
Cleckheaton Road, Low Moor
Bradford, West Yorkshire BD2 3JT
ROYAUME-UNI

Date of mailing *(day/month/year)* 23 August 2007 (23.08.2007)	
Applicant's or agent's file reference MP/3-22379	**IMPORTANT NOTICE**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2007/050084	04 January 2007 (04.01.2007)	18 January 2006 (18.01.2006)

Applicant: CIBA SPECIALTY CHEMICALS HOLDING INC. et al

1. **ATTENTION**: For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does apply**, please see Form PCT/IB/308(Second and Supplementary Notice) (to be issued promptly after the expiration of 28 months from the priority date).

2. Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93*bis*.1. The International Bureau has effected that communication on the date indicated below:
26 July 2007 (26.07.2007)

   None

   In accordance with Rule 47.1(c-*bis*)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

3. The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93*bis*.1 :

   CH, LU, SE, TZ, UG

   In accordance with Rule 47.1(c-*bis*)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

4. **TIME LIMITS for entry into the national phase**

   For the designated Office(s) listed above, and unless a demand for international preliminary examination has been filed before the expiration of **19 months** from the priority date (see Article 39(1)), the applicable time limit for entering the national phase will, **subject to what is said in the following paragraph,** be **20 MONTHS** from the priority date.

   In practice, **time limits other than the 20-month time limit** will continue to apply, for various periods of time, in respect of certain of the designated Offices listed above. For **regular updates on the applicable time limits** (20 or 21 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at http://www.wipo.int/pct/en/index.html.

   It is the applicant's **sole responsibility** to monitor all these time limits.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer
Yolaine Cussac

Facsimile No. +41 22 338 82 70

t11.pct@wipo.int

PATENT COOPERATION TREATY

PCT/EP2007/050084

RECEIVED
17 APR 2008

From the INTERNATIONAL BUREAU

PCT

To:

CIBA SPECIALTY CHEMICALS HOLDING PLC
Patent Department
P.O. Box 38
Cleckheaton Road, Low Moor
Bradford, West Yorkshire BD2 3JT
ROYAUME-UNI

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

Date of mailing *(day/month/year)*
04 April 2008 (04.04.2008)

Applicant's or agent's file reference
MP/3-22379

IMPORTANT NOTIFICATION

International application No.
PCT/EP2007/050084

International filing date *(day/month/year)*
04 January 2007 (04.01.2007)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address
CIBA SPECIALTY CHEMICALS HOLDING INC.
Patent Department
Klybeckstrasse 141
CH-4057 Basel
Switzerland

State of Nationality: CH
State of Residence: CH
Telephone No.: +41 1274-4174461
Facsimile No.: +41 1274-417406
Teleprinter No.:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address
CIBA HOLDING INC.
Patent Department
Klybeckstrasse 141
CH-4057 Basel
Switzerland

State of Nationality: CH
State of Residence: CH
Telephone No.: +41 1274-4174461
Facsimile No.: +41 1274-417406
Teleprinter No.:

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☐ the International Searching Authority
☐ the International Preliminary Examining Authority
☒ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 89 70

Authorized officer
Wittmann-Regis Agnes
e-mail pt06.pct@wipo.int
Telephone No. +41 22 338 74 06

Form PCT/IB/306 (October 2005)

1/DL0LV1I30

204

205

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 08-083545- -00000-0000
Fecha: 2008-08-12 14:46:44 Dep: 2020 NUECREACIONI
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 204

Industria y Comercio
SUPERINTENDENCIA

REQUISITOS MINIMOS PARA ADMISION A TRAMITE PCT

PATENTE DE INVENCION [X] MODELO DE UTILIDAD [ ]

- Indicación de que se solicita la concesión de una patente [X]
- Datos de identificación del solicitante o de la persona que presenta la solicitud [X]
- Descripción de la invención [X]
- Dibujos de ser estos pertinentes [ ]
- Comprobante de pago de las tasas establecidas [X]

COMPLETA [ ] INCOMPLETA [ ]

DISEÑO INDUSTRIAL [ ]

- Indicación de que se solicita el registro de Diseño Industrial [ ]
- Datos de identificación del solicitante o de la persona que presenta la solicitud [ ]
- Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño [ ]
- Comprobante de pago de las tasas establecidas [ ]

COMPLETA [ ] INCOMPLETA [ ]

ESQUEMA DE TRAZADO [ ]

- Indicación de que se solicita el registro de un Esquema de Trazado [ ]
- Datos de identificación del solicitante o de la persona que presenta la solicitud [ ]
- Representación gráfica del esquema trazado [ ]
- Comprobante de pago de las tasas establecidas [ ]

COMPLETA [ ] INCOMPLETA [ ]

Marlu Ruiz

Firma Responsable

Fecha 12 AGO/08

Carrera 13 No. 27-00 Piso 5, 7 y 10
Conmutador: 3 82 08 40
Fax: 350 52 20
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia

REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
ESCOBAR URIBE JIMENA

REFERENCIA	Radicación No.	8 83545
	Solicitud internacional	PCT/EP2007/050084
	Fecha inicio fase nacional	18/08/2008
	Trámite	11
	Evento	378
	Actuación	430
	Oficio No.	11313

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

1. La solicitud no contiene el poder debidamente otorgado, con el lleno de los requisitos exigidos por los artículos 63 y subsiguientes del Código de Procedimiento Civil. Adicionalmente, deberá presentar el documento que acredita la existencia y representación legal de la sociedad solicitante, cuando ésta fuere persona jurídica.

2. El solicitante debe presentar un nuevo titulo que permita identificar la materia de la cual trata la solicitud, ya que el titulo relacionado no se encuentra con la precisión necesaria para identificar claramente el objeto de la solicitud de patente. (Regla 4.3 PCT, Art 26-27 D-486, Circular única 5.2.9)

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

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

ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la división de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de fecha 05 SET. 2008
jfernand