

DOCTORA:

EDNA MARCELA RAMÍREZ OROZCO

DIRECTORA NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

E. S. D.

REF. EXPEDIENTE No.: NC2019/0000846.
FORMULACIÓN AGRÍCOLA QUE
SOLICITUD PATENTE: COMPRENDE ACEITE DE LINAZA,
PARTÍCULAS SUSPENDIDAS DE MINERALES
SOLICITANTE: DE ARCILLA Y UN TENSIOACTIVO.
CROP ENHANCEMENT, INC.

RESPUESTA A REQUERIMIENTO OFICIAL **OFICIO NO. 16892** NOTIFICADO EL 17
OCTUBRE DE 2023.

CLAUDIA LUCIA CARO RAMIREZ, mayor de edad, domiciliada en Bogotá D.C.,
identificada con cedula No 40.017.374, en mi condición de apoderada de **CROP
ENHANCEMENT, INC**, por el presente escrito y estando dentro del término legal
para hacerlo, doy respuesta al oficio arriba referenciado, de acuerdo con lo
siguiente:

En respuesta al oficio No. 16892, a continuación, encuentran:

- i. Respuesta a los puntos del requerimiento
 - Respuesta punto por punto a los requerimientos de del
examinador.
- ii. Adjunto a este memorial se presentan los siguientes documentos
 - Nuevo capítulo reivindicatorio en limpio.
 - Comprobante de pago correspondiente a las modificaciones al
capítulo reivindicatorio.
 - Patente US 6.130.256
 - Patente US 5.292.908

1. Excepción de patentabilidad.

- Manifiesta el examinador que el objeto de la reivindicación 4 no es patentable, toda vez que, que se refiere a un producto vegetal. Conforme a lo establecido en el artículo 20 de la decisión 486, las plantas no serán patentables.

El solicitante ha eliminado la reivindicación 4. Entiende el solicitante que la objeción ha sido subsanada.

2. Determinación de Estado de la técnica:

Como resultado del examen de patentabilidad el examinador encontró los siguientes documentos relevantes:

Ítem	Documento	Título	Fecha de publicación
D4	US20110275516	<i>"Stabilized agricultural oil dispersions"</i>	10 de noviembre de 2011.
D5	WO2013171525	<i>"Carriers for pesticides and process for forming adherent pesticide film"</i>	21 de noviembre de 2013

3. Examen de patentabilidad

Nivel inventivo

Inicia el examinar el examen de nivel inventivo comparando las características técnicas de la reivindicación 1 de la presente invención (NC2019/0000846) con la materia revelada en D4 y D5. Luego de esta comparación manifiesta el examinador que D5 se considera el estado de la técnica más cercano a la invención definida en la reivindicación 1.

Manifiesta el examinador que la principal diferencia entre la invención definida en D5 y la presente invención radica en aumentar la proporción de arcilla,

seleccionarla específicamente de partículas de bentonita que no están orgánicamente modificadas y no incluir pesticidas.

Manifiesta el examinador que *"no se observa un efecto técnico asociado a aumentar la proporción de arcilla y seleccionarla específicamente de partículas de bentonita que no están orgánicamente modificadas, y no incluir pesticidas; porque las pruebas presentadas junto con el radicado N° NC2019/0000846 el 17 de julio de 2023, en la declaración de Damian Hajduk, PhD (uno de los inventores), realiza estudios comparativos contra ausencia total de tratamiento, por lo que no es posible atribuir puntualmente el efecto observado a la proporción de arcilla empleada y la naturaleza química específica que se está reclamando, adicionalmente es ampliamente conocido* por la persona del oficio versada en la materia que los aceites vegetales como el aceite de linaza tienen aplicación como biopesticidas y se ha probado su acción específica contra distintas clases de plagas, por lo que es claro que el aceite por sí solo ya proporciona protección frente a las plagas y los datos presentados en la declaración adjunta no son concluyentes con respecto al efecto técnico de la formulación que actualmente se reclama"* (tomado del Oficio N° 16892). *cita el examinador tres documentos para soportar la afirmación relacionada con el conocimiento de la diferencia técnica planteada por el examinador.

Plantea entonces el examinador que *el problema técnico objetivo que pretende resolver esta invención se puede formular así: ¿Cómo modificar la formulación conocida en D5 con el fin de proporcionar una formulación alternativa?* (tomado del Oficio N° 16892).

Manifiesta el examinador que el incluir una proporción mayor de arcilla, ya está divulgado en D4 cita el examinador la reivindicación 1, Párr. 0024, 0026 y 0038 de D4.

Manifiesta entonces el examinador que la persona normalmente versada en la materia, estaría motivada a incluir una mayor proporción de partículas minerales

de arcilla de D4 en la formulación de D5, para así llegar al objeto de la reivindicación 1. Por lo cual se considera obvia.

Las reivindicaciones 2 a 3 no mencionan alguna característica que aporten al nivel inventivo de la invención.

El solicitante quisiera manifestar su desacuerdo con las objeciones planteadas por el examinador. El solicitante quisiera resaltar que el capítulo reivindicatorio está dirigido a proteger una formulación agrícola no tóxica que reivindica una suspensión líquida concentrada que comprende:

- i) aceite de linaza donde el aceite de linaza se encuentra entre el 40% al 90% en peso respecto a la formulación,
- ii) partículas de bentonita suspendida que se encuentran entre 10% a 40% en peso respecto a la formulación donde la bentonita no está orgánicamente modificada;
- iii) un tensoactivo se encuentra entre 0.1% as 15% en peso respecto a la formulación;
- iv) donde la formulación no contiene pesticidas.

Como se analizó y mostro anteriormente (en la anterior respuesta al oficio N° 3176), el aceite de linaza es un aceite secante y forma una capa curada al secarse (P.6, líneas 16 a 31 del capítulo descriptivo tal y como se modificó el 17 de julio de 2023). Debido a que las partículas de arcilla de bentonita están suspendidas en el aceite de linaza, el recubrimiento curado sobre la superficie de la planta comprende las partículas de arcilla de bentonita suspendidas. Esta formulación agrícola a base de aceite de linaza forma una capa de barrera no tóxica en la superficie de la planta que disuade a las plagas incluso en ausencia de pesticidas. Por ejemplo, el recubrimiento curado que comprende las partículas de arcilla de bentonita suspendidas altera la presentación sensorial de la superficie de la planta a la plaga (en otras palabras, cambia la forma en que la plaga percibe la superficie de la

planta). Ver P.23, líneas 22 a 29 del capítulo descriptivo tal y como se modificó el 17 de julio de 2023.

La formulación tal y como se reivindica no habría sido obvia a la luz de las enseñanzas, bien sea tomadas de forma individual o en combinación de D5 y D4.

Con respecto a D5.

El examinador considera que D5 es el estado de la técnica más cercano. D5 describe el uso de aceites secantes como portador de formador de películas polimerizables para pesticidas (P.2, líneas 23-32; reivindicación 1, de D5). En D5, se utiliza un aceite secante como portador del pesticida (P.2, líneas 30-32). D5 enseña que las formulaciones se pueden aplicar como suspoemulsiones de aceite-agua (P.2, líneas 22-27). D5 también enseña que la suspoemulsión puede comprender adicionalmente un aditivo tal como un emulsionante, un agente antiespumante y un agente tixotropizante (en otras palabras, un agente espesante). Un agente tixotropizante incluye un aditivo mineral tal como Attagel 50 (una arcilla de atapulgita) (P.5, líneas 24-35). Los Ejemplos de D5 proporcionan ejemplos específicos de formulaciones en suspoemulsión, incluidas algunas que comprenden Attagel 50 en cantidades del 2 % en peso o menos (Ejemplos 1, 2 y 5-7).

Para el solicitante es claro que D5 no enseña:

- i) aceite de linaza donde el aceite de linaza se encuentra entre el 40% al 90% en peso respecto a la formulación,
- ii) partículas de bentonita suspendida que se encuentran entre 10% a 40% en peso respecto a la formulación donde la bentonita no está orgánicamente modificada;
- iii) un tensoactivo se encuentra entre 0.1% as 15% en peso respecto a la formulación; y
- iv) donde la formulación no contiene pesticidas.

A continuación, se explicará con más detalle:

i. D5 no enseña el aceite de linaza en la cantidad reivindicada.

El único ejemplo específico que incluye aceite de linaza en D5 es el Ejemplo 5 que describe una suspoemulsión de cobre en la que el aceite de linaza está presente en sólo un 12-21 % en peso. Por tanto, D5 no enseña una formulación que comprenda aceite de linaza en una cantidad del 40-90% en peso como lo requieren las presentes reivindicaciones.

ii. D5 no enseña una composición que comprende partículas de arcilla de bentonita.

D5 tampoco describe una composición que comprenda partículas de arcilla de bentonita en una cantidad del 10 al 40% en peso, como se reivindica en la presente invención. En cambio, D5 describe el uso de arcilla de atapulgita como agente tixotrópico en la suspoemulsión de aceite y agua. Es importante resaltar que el Ejemplo 5 de D5 (el único ejemplo que describe una formulación que contiene aceite de linaza) describe una formulación con óxido de cobre al 13-30 % en peso y Attagel 50 al 0,5-2 % en peso. Resulta muy claro para el solicitante que, D5 no describe la inclusión de partículas de arcilla de bentonita suspendidas en aceite de linaza en una cantidad de entre 10% - 40% en peso como se reivindica. Resulta entonces claro que la persona versada en la materia no habría tenido ningún motivo para sustituir la atapulgita D5 por bentonita.

Además, D5 incluye atapulgita (Attagel 50) en cantidades del 2% en peso o menos (Ejemplos 1, 2 y 5-7). Nuevamente, cabe señalar que D5 describe el propósito de la atapulgita como espesante. La cantidad de atapulgita en D5 es aproximadamente 5 veces menor que la cantidad mínima de bentonita requerida por las presentes reivindicaciones. La persona versada en la materia no habría tenido motivos razonables para haber aumentado la cantidad de bentonita al menos 5 veces en comparación con la cantidad de arcilla de atapulgita enseñada

en D5, para cumplir con la limitación que se define en las presentes reivindicaciones. Para aumentar cinco veces la cantidad de arcilla sería necesario disminuir la cantidad de uno de los otros componentes y, por lo tanto, cambiar fundamentalmente la naturaleza de la composición de D5. Además, dado que Attagel 50 de D5 se usa como agente espesante (o agente tixotropizante), de acuerdo con dicha característica es claro que la persona versada en la materia no habría aumentado la cantidad del agente espesante (Attagel 50) al menos 5 veces, ya que eso habría aumentado el espesor de la formulación, lo que tienen el efecto negativo de aumentar la dificultad de pulverizar o aplicar de otro modo la formulación de D5.

Respecto a la combinación de enseñanzas de D5 y D4

El examinador sostiene que la persona versada en la materia habría aumentado la cantidad de partículas de mineral de arcilla en D5 basándose en las enseñanzas de D4. D4 describe dispersiones de aceite que comprenden un disolvente orgánico, un ingrediente activo (tal como un herbicida o pesticida), un polímero capaz de formar enlaces de hidrógeno y un modificador de reología (párrafos [0012] y [0013] de D4). El propósito de la dispersión de D4 es administrar un ingrediente agroquímico activo (como un herbicida o un pesticida) en forma fluida y requiere un polímero/oligómero capaz de unirse al hidrógeno en combinación con un modificador de la reología de arcilla o sílice para mejorar la "*estabilidad física a formulaciones en dispersión oleosa de productos agroquímicos (physical stability to oil dispersion formulations of agrochemical products)*" (párrafo [0012], de D4).

La formulación reivindicada en la presente invención (NC2019/0000846) requiere partículas minerales de arcilla bentonita en un porcentaje en peso específico respecto de la formulación. Específicamente, las reivindicaciones requieren que la partícula mineral de arcilla bentonita esté presente en una cantidad del 10 al 40% en peso de la formulación. El porcentaje en peso (p/p) es el peso del soluto (en gramos, por ejemplo) dividido por el peso de la solución (en gramos, por ejemplo) multiplicado por 100. **No** se describe en D4 el *porcentaje en peso* del modificador

de reología. En lugar de ello, D4 describe rangos de concentración (en gramos por litro) para los componentes de las dispersiones oleosas. Por ejemplo, D4 enseña que el modificador de reología y el polímero/oligómero están presentes de 1 a 200 g/l, lo que se calcula en 0,1 a 20 % p/v. El examinador parece suponer que el porcentaje en peso con respecto al volumen (p/v) es el mismo que el porcentaje en peso (o peso con respecto al peso; p/p). **No lo es.** No hay información en D4 sobre los porcentajes en peso de los componentes de la dispersión en aceite, incluido el modificador de reología.

Incluso suponiendo, únicamente en aras de argumentar, que la persona versada en la materia decidiera utilizar el modificador reológico de D4 en la composición de D5, D4 enseña el uso de una organoarcilla que es una partícula de arcilla de bentonita modificada orgánicamente. Por el contrario, las presentes reivindicaciones requieren que las partículas de arcilla bentonita no estén modificadas orgánicamente. El Examinador descarta esta distinción argumentando que las arcillas modificadas orgánicamente y la bentonita no modificada son equivalentes técnicos conocidos.

Esto último es incorrecto. Sólo las arcillas modificadas orgánicamente son dispersables en fluidos no acuosos (en ausencia de un tensioactivo) y, por tanto, se utilizan a menudo para proporcionar un efecto espesante. Si bien la adición de un sólido, como partículas minerales de arcilla no modificadas, a un líquido puede dar como resultado cierto aumento en la viscosidad, la magnitud de ese aumento depende del grado en que el sólido está disperso en el líquido. Una dispersión deficiente o una dispersión inestable tendrá un efecto mínimo sobre la viscosidad. Por lo tanto, las arcillas no modificadas y las arcillas modificadas orgánicamente no son equivalentes técnicos. Por el contrario, cada uno de ellos tiene diferentes dispersabilidades en los aceites y, por lo tanto, tienen diferentes efectos sobre la viscosidad o el espesamiento de una formulación específica.

para facilitar el entender que sólo las arcillas modificadas orgánicamente son dispersables en fluidos no acuosos, agradecemos referirse a los anexos 1 y 2

(Patentes de EE.UU. Nos. 6.130.256 y Patente de EE.UU. N° 5.292.908) que enseñan que las arcillas no modificadas no son dispersables en fluidos no acuosos y que sólo las organoarcillas son adecuadas como modificadores de la reología:

Por ejemplo, en la columna 1 líneas 13 a 24 de la patente US 6,130,256 menciona lo siguiente:

It is well known that organic compounds containing a cation will react with a clay under favorable conditions by ion exchange to form an organophilic clay. *Such clay modification results in a product **which unlike clay** is dispersible in non-aqueous fluids to change fluids characteristics such as viscosity.* It is also known in the art that such organophilic clays can be used to modify the viscosity (thicken) of a variety of organic compositions including inks, greases, drilling fluids, paints and other similar products. (columna 1 líneas 13 a 24 de la patente US6,130,256, cursiva y negrita fuera del texto original).

Es bien sabido que los compuestos orgánicos que contienen un catión reaccionarán con una arcilla en condiciones favorables mediante intercambio iónico para formar una arcilla organófila (organoarcillas). *Dicha modificación de la arcilla da como resultado un producto que, **a diferencia de la arcilla**, es dispersable en fluidos no acuosos para cambiar las características de los fluidos, como la viscosidad.* También se sabe en la técnica que dichas arcillas organófilas se pueden usar para modificar la viscosidad (espesar) de una variedad de composiciones orgánicas que incluyen tintas, grasas, fluidos de perforación, pinturas y otros productos similares. (traducción libre de la columna 1 líneas 13 a 24 de la patente US6,130,256, cursiva, negrita y paréntesis aclaratorio fuera del texto original).

Así mismo la patente US 5,292,908. Describe lo siguiente

Because the bentonite powder which is merely purified *can not be dispersed in organic-solvents*, ***it is not suitable as a rheological adjuster for liquid products containing an organic solvent***, such as alkyd resin coatings or other synthetic resin coatings, printing inks, and sealants. Hence, the purified bentonite is rendered organophilic by combining with a quaternary ammonium cation (see U.S. Pat. No. 2,531,427), a composite of a quaternary ammonium cation and a nonionic organic compound... (columna 1 líneas 44 a 53 de la patente US5,292,908, cursiva y negrita fuera del texto original).

Debido a que el polvo de bentonita simplemente purificado *no se puede dispersar en solventes orgánicos*, ***no es adecuado como ajustador reológico para productos líquidos que contienen un solvente orgánico***, tales como recubrimientos de resina alquídica u otros recubrimientos de resina sintética, tintas de impresión y selladores. Por lo tanto, la bentonita purificada se vuelve organófila combinándola con un catión de amonio cuaternario (ver la patente de EE.UU. n° 2.531.427), un compuesto de un catión de amonio cuaternario y un compuesto orgánico no iónico...(traducción libre de columna 1 líneas 44 a 53 de la patente US5,292,908, cursiva y negrita fuera del texto original).

La formulación reivindicada utiliza una partícula mineral de arcilla de bentonita no modificada con un tensioactivo y, como tal, es al menos parcialmente dispersable en la formulación de aceite. Sin embargo, el propósito de la partícula de mineral de arcilla en la formulación reivindicada no es aumentar la viscosidad de la formulación tal como el modificador de reología en D4 o el espesante en D5. De hecho, cualquier aumento de la viscosidad es un inconveniente porque aumenta la dificultad de manipulación de la formulación reivindicada. Además, la persona versada en la materia no habría sustituido una partícula de mineral de arcilla no modificada por el espesante de D5/D4 porque la partícula de arcilla no modificada no es fácilmente dispersable en formulaciones de aceite, ni tampoco se usa la arcilla no modificada en la técnica como espesante o como modificador de

reología. Las arcillas modificadas orgánicamente se utilizan tradicionalmente como espesantes en aceites, mientras que las arcillas no modificadas no.

Como tal, la persona versada en la materia no habría considerado la arcilla orgánica de D4 como un **"equivalente técnico"** de la arcilla bentonita no modificada. Tienen diferentes propósitos y se usan en diferentes tipos de formulaciones, en las que logran esos propósitos. Por lo tanto, incluso si la persona versada en la materia modificara D5 con la organoarcilla de D4, esto no sería equivalente a la formulación tal y como se reivindica en la presente invención. Como tal, incluso combinar las enseñanzas de D5 y D4 como argumenta el Examinador no conduciría a la formulación tal y como se reivindica.

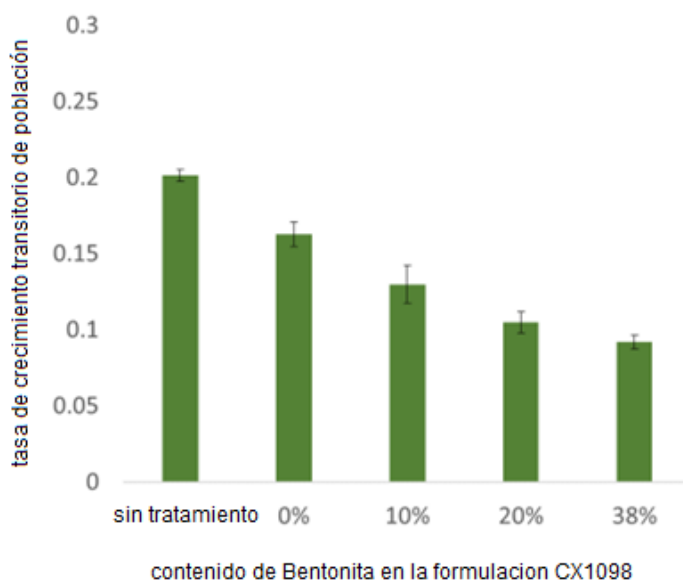
El efecto disuasorio de plagas de la formulación reivindicada se debe a la presencia de partículas de arcilla bentonita en la formulación de aceite de linaza; El aceite de linaza en sí no tiene los mismos efectos disuasorios de plagas.

En apoyo de efectos inesperados, se presentó la Declaración del Dr. Damian Hajduk (uno de los inventores) con la última respuesta al oficio N° 3173 . En la Declaración, el Dr. Hajduk describe experimentos en los que se rociaron plantas con una formulación que cumplía con las presentes reivindicaciones (denominada "CropCoat") o con agua, y se dejaron secar (Declaración, págs. 1-3). La formulación de CropCoat descrita en la Declaración del inventor incluye 54% p/p de aceite de linaza crudo, 38,2% p/p de bentonita y los tensioactivos Jarfactant 325N, Span 85 y Methocel E-15 LV, y no incluye pesticidas (Declaración, Tabla uniendo págs. 1-2). Los datos de la Declaración muestran que cuando la formulación se aplicó a las superficies de las hojas de las plantas y formó una capa curada, la capa alteró el comportamiento de las plagas y, por lo tanto, disuadió el daño de las mismas *en ausencia de un pesticida*.

El Examinador descarta la relevancia de estos datos argumentando que no es posible atribuir un efecto a las partículas minerales de arcilla ya que el trabajo

experimental en la Declaración comparó el efecto de la formulación CropCoat contra la ausencia de tratamiento (agua). El Examinador afirma que el efecto de la formulación se debe a la presencia de un aceite vegetal que tiene una conocida "acción como pesticida".

Para respaldar aún más el efecto de la formulación reivindicada, consulte a continuación los datos complementarios que muestran que una formulación que comprende aceite de linaza por si sola (sin partículas de arcilla de bentonita) tuvo un efecto disuasivo de plagas mínimo, contradiciendo así la posición del Examinador de que el efecto de la formulación reivindicada es debido únicamente a la presencia del aceite vegetal que tiene "una conocida acción como pesticida". Específicamente, el siguiente gráfico muestra el efecto de las formulaciones de aceite de linaza con concentraciones variables de bentonita (de 0% a 38%) sobre el crecimiento de la población de pulgón (*B. brassicae*) (tasa de crecimiento transitoria) durante un período de 7 días en repollo.



La composición de la formulación probada (CX1098) se resume en la siguiente tabla:

	% Aceite de linaza crudo	% Bentonita	% tensoactivos
CX1098 0%	91.95	0%	1% Jarfactant 325 2% Span 85 1% Break Thru SP133
CX1098 10%	81.95	10	1% Jarfactant 325 2% Span 85 1% Break Thru SP133
CX1098 20%	71.95	20	1% Jarfactant 325 2% Span 85 1% Break Thru SP133
CX1098 38%	53.95	38	1% Jarfactant 325 2% Span 85 1% Break Thru SP133

El tratamiento del repollo con la formulación que comprende 91,95 % de aceite de linaza y 0 % de bentonita ("0 %" en el gráfico; CX1098 0 % en la tabla) mostró un cambio mínimo en el crecimiento transitorio de la población de pulgones en el repollo en comparación con el repollo no tratado (desde 0,2 para el repollo sin tratar hasta aproximadamente 0,16 para la formulación de 0 % de bentonita/91,95 % de aceite de linaza). Por el contrario, la adición de bentonita tuvo un efecto dependiente de la concentración en la disminución de la tasa de crecimiento transitorio. Como se muestra en el gráfico, las formulaciones de aceite de linaza que comprenden 20 % y 38 % de partículas de bentonita disminuyeron la tasa de crecimiento transitorio de la población en aproximadamente un 50 % en comparación con el repollo sin tratar (0,2 para el repollo sin tratar en comparación con aproximadamente 0,1 para la formulación de aceite de linaza con 53,95 % 38 % de bentonita).

Estos datos son evidencia de que una formulación que comprende 91,95% de aceite de linaza y nada de bentonita casi no tuvo efecto disuasivo de plagas. Esto contradice la posición del Examinador de que la formulación de D5 en sí misma habría tenido un efecto disuasorio de plagas en ausencia de pesticidas y que aumentar la cantidad de partículas minerales de arcilla no tendría ningún efecto técnico. Estos datos son una prueba más de que el efecto disuasorio de plagas de

la composición reivindicada, incluso en ausencia de un pesticida convencional, es sorprendente he inesperada.

La presente solicitud enseña que la formulación de aceite reivindicada disuade las plagas porque altera las características de la superficie de la planta, repeliendo así las plagas incluso sin la presencia de pesticidas, esto es más claro aún en el siguiente apartado de la descripción:

En determinadas modalidades, la formulación agrícola basada en aceite secante puede usarse para formar una composición no tóxica del recubrimiento de barrera cuando se aplica a un objetivo agrícola, por ejemplo, una planta, una fruta, un vegetal y similares. Por ejemplo, en modalidades, una formulación puede ser rociada sobre superficies de un objetivo agrícola, por ejemplo, superficies de frutas o vegetales o plantas (troncos, follaje, hojas, semillas, bayas, nueces, raíces, ramas, y similares), *donde la formulación puede estar libre de ingredientes tóxicos tales como plaguicidas*. En modalidades, las composiciones no tóxicas del recubrimiento de barrera pueden impedir el daño por plagas **debido a una alteración del reconocimiento sensorial de la superficie vegetal; por ejemplo, la superficie vegetal tratada puede tener diferencias en cuanto a la energía superficial, ser resbaladiza, compatibilidad con estructuras fisiológicas de las patas de insectos, textura superficial, perfil de olores, apariencia visual, y firma de calor en comparación con una superficie vegetal no tratada**. Esta presentación sensorial alterada puede cambiar los comportamientos de insectos y animales de manera que no escojan comerse o dañar de cualquier otra manera la planta tratada (página 23 líneas 17 a 29 del capítulo descriptivo tal y como se modificó el 17 de julio de 2023, cursiva y negrita fuera del texto original énfasis añadido)

Los datos complementarios presentados anteriormente son evidencia adicional de que la formulación reivindicada que incluye partículas de bentonita tiene un efecto profundo, libre de pesticidas y dependiente de la concentración, para disuadir

plagas que no podría haberse predicho a partir de la combinación de D5 y D4. Por estas diversas razones, las presentes reivindicaciones son novedosas y no obvias con respecto a D4 o D5 tomados de forma individual o en cualquier combinación.

Por todo lo dicho, solicitamos que la Superintendencia de Industria y Comercio admita las modificaciones y argumentos que se han facilitado, las cuales no amplían materia y subsanan las objeciones realizadas por el examinador referentes a la novedad y el nivel inventivo. Asimismo, solicitamos que continúe el trámite con normalidad y se proceda con la concesión del Derecho sobre la Patente de la referencia.

Para efectos de notificaciones, recibiré estas vía internet al correo electrónico claudia.caro@ponsip.com, en la secretaría de esa Dirección y/o en la de la Delegatura de Propiedad Intelectual o en mi oficina de abogados de la Calle 94 A No 11A-32 Oficina 306 de la ciudad de Bogotá.

Agradezco su atención.



CLAUDIA LUCIA CARO RAMIREZ

CC No 40.017.374 de Tunja
T.P. No 36.448 del C.S de la J.
Adjunto lo anunciado.

Reivindicaciones

1. Una formulación agrícola no tóxica que comprende una suspensión líquida concentrada que incluye un aceite secante, partículas de minerales de arcilla y un tensoactivo,
5 donde las partículas de minerales de arcilla están suspendidas en el aceite secante, y donde las partículas de mineral de arcilla corresponden a partículas de bentonita y donde las partículas de bentonita no están orgánicamente modificadas;
 donde el aceite secante se encuentra entre el 40% al 90% en peso respecto a la formulación;
 donde el aceite secante corresponde a aceite de linaza;
10 donde las partículas de minerales de arcilla se encuentran entre 10% a 40% en peso respecto a la formulación, y
 donde el tensoactivo se encuentra entre 0.1% as 15% en peso respecto a la formulación y se selecciona del grupo que consiste en alcohol etoxilado, un éster graso de sorbitán, un alquilpoliglucósido, un copolímero de óxido de etileno/óxido de propileno (EO/PO), guar, xantana,
15 lecitina de soya, o un estearato de sorbitán etoxilado; y
 donde la formulación no contiene pesticidas.
2. La formulación de la reivindicación 1, en donde el aceite secante corresponde a aceite de linaza crudo o aceite de linaza hervido.
20
3. La formulación de la reivindicación 1, en donde las partículas de minerales de arcilla se encuentran entre un 20% a un 35% en peso respecto a la formulación.



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT: 800.176.089-2

COMPROBANTE DE RECAUDO SISTEMA SIPI

Radicado: NC2024/0002680
Recibo: 24-15140
Fecha: 01/03/2024

CLAUDIA LUCIA CARO RAMIREZ
CC: 40.017.374
Pago PSE No: 937049
CUS: 486743088

NC Modificación a las reivindicaciones
Request on Patente PCT NC2019/0000846

Detalle del pago

Id.	Rentístico	Concepto y Servicio	Cant.	Val. Unit.	Subtotal
1	50005-01-03	Modificaciones / Correcciones al registro Patente PCT (DESCUENTO INTERNET)	1	\$ 215,000	\$ 215,000
TOTAL					\$ 215,000



US006130256A

United States Patent [19]
Nae

[11] Patent Number: 6,130,256
[45] Date of Patent: Oct. 10, 2000

[54] **ORGANOCLAY THICKENER COMPATIBLE WITH SYSTEM TO BE THICKENED**

[75] Inventor: Hemi Nae, Princeton Junction, N.J.

[73] Assignee: Rheox, Inc., Hightstown, N.J.

[21] Appl. No.: 08/066,773

[22] Filed: May 7, 1993

[51] Int. Cl.⁷ B01J 13/00; C08J 3/09; C09D 11/06

[52] U.S. Cl. 516/34; 106/31.3; 106/31.57; 507/901; 508/136; 516/101; 556/173

[58] Field of Search 252/309, 315.2, 252/28; 507/901; 556/173; 106/22 E, 23 E, 28 R, 31.34, 31.57; 516/31, 101, 34; 508/136

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,622,987	12/1952	Ratcliffe		252/315.2 X
2,859,234	11/1958	Clem		556/173
4,105,578	8/1978	Finlayson et al.		252/315.2
4,193,806	3/1980	Finlayson		106/20
4,208,218	6/1980	Finlayson		252/315.2 X

4,410,364	10/1983	Finlayson et al.		106/20
4,412,018	10/1983	Finlayson et al.		252/315.2 X
4,434,075	2/1984	Mardis et al.		252/315.2
4,450,095	5/1984	Finlayson		252/315.2
4,664,820	5/1987	Magavran et al.		252/28
5,178,672	1/1993	Miller		106/28 R

OTHER PUBLICATIONS

NLGI lubricating grease guide, 1984 revised 1987, pp. 2.14 to 2.17, 4.12 to 5.01.
Boner, Modern Lubricating greases, 1976 pp. 2.26–2.27, 3.16 to 3.19 and 6.12 to 6.13.

Primary Examiner—Richard D. Lovering
Attorney, Agent, or Firm—Michael J. Cronin

[57] **ABSTRACT**

An organophilic clay thickener for natural oil systems comprising the reaction product of a smectite-type clay and an organic cation in an amount of from about 75% to about 150% of the cation exchange capacity of the smectite-type clay. Said organophilic clay comprising at least one naturally occurring, resulting in increased efficiency as a thickener in natural oil systems.

10 Claims, 2 Drawing Sheets

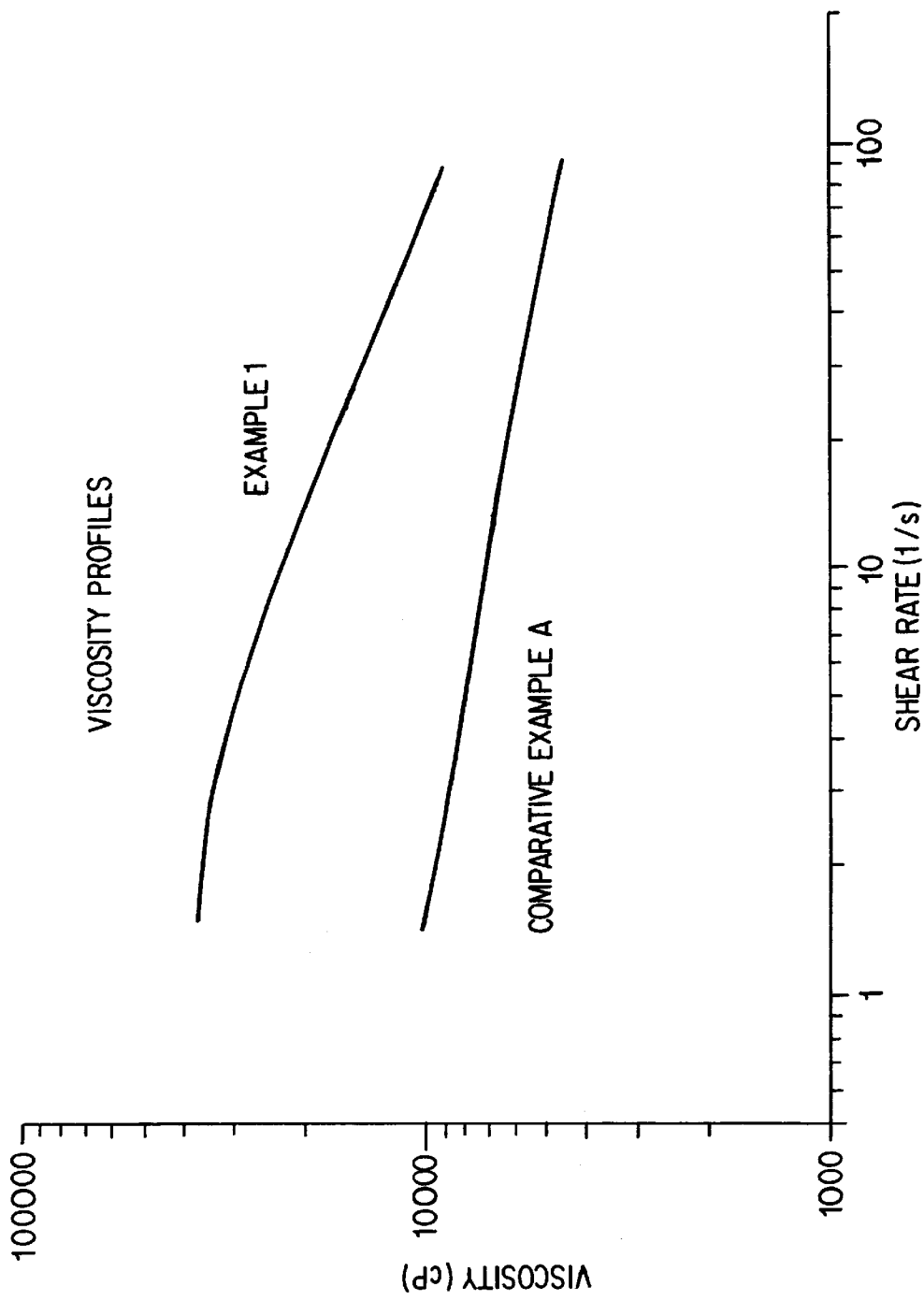


FIG. 1

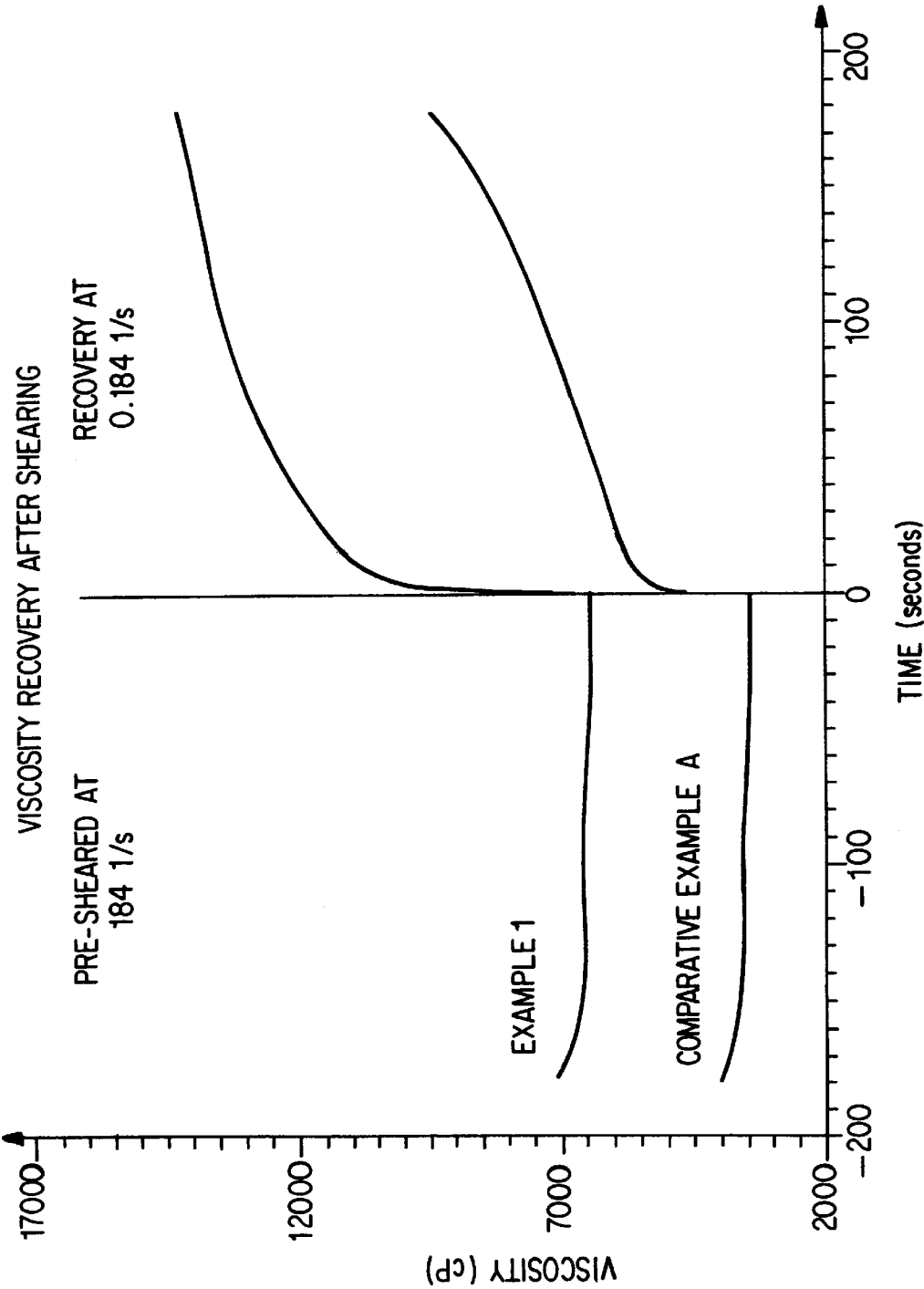


FIG. 2

ORGANOCLAY THICKENER COMPATIBLE WITH SYSTEM TO BE THICKENED

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention relates to organophilic clay thickeners which are dispersible in non-aqueous fluids to thicken such fluids by forming a gel therein or otherwise modifying the viscosity of such fluids. The invention also pertains to a process for preparing these organophilic clay gellants, and to non-aqueous fluid compositions including the same.

It is well known that organic compounds containing a cation will react with a clay under favorable conditions by ion exchange to form an organophilic clay. Such clay modification results in a product which unlike clay is dispersible in non-aqueous fluids to change fluids characteristics such as viscosity. It is also known in the art that such organophilic clays can be used to modify the viscosity (thicken) of a variety of organic compositions including inks, greases, drilling fluids, paints and other similar products. See for example, U.S. Pat. No. 2,966,506 and the book *Clay Mineralogy*, 2nd Ed., 1968, R. E. Grim (McGraw Hill Book Company).

It is also well known that such complexes may function to thicken polar or non-polar petroleum based solvents, depending on the substituents on the organic salt. J. W. Jordan, in "Proceedings of the 10th National Conference on Clays and Clay Minerals" (1963), discusses a wide range of applications of organophilic clays.

In some situations the efficiency of organophilic clays can be further improved by adding a low molecular weight polar organic material to the composition. Such polar organic materials have been called dispersants, dispersion aids, solvating agents and the like. The most efficient polar materials for use as such have been found to be low molecular weight alcohol and ketones, particularly methanol and acetone. See for example U.S. Pat. Nos. 2,677,661, 2,704,276, 2,833,720, 2,879,229 and 3,294,683. The use of such dispersion aids has in other situations been found to be unnecessary when using specially designed organoclays. See U.S. Pat. Nos. 4,105,578 and 4,208,218.

Furthermore, U.S. Pat. Nos. 3,977,897, 4,382,868 and 4,464,274 describe the preparation of preactivated organophilic clay gellants, used to thicken organic compositions wherein the activators are admixed with the organophilic clays.

More recently, organophilic clay gellants have been developed which are the reaction products of smectite-type clays with organic cations and organic anion combinations. These gellants have the advantage of being effectively dispersible in particular organic compositions. An illustrative patent which describes such improved organophilic clay gellants is U.S. Pat. No. 4,412,018.

There is today a growing demand for products based on naturally occurring oils such as soybean oil, safflower oil, corn oil, palm oil and the like, to replace organic solvents based on petroleum derivatives such as toluene, xylene or mineral spirits. Such solvents have more beneficial properties from environmental standpoints and in many ways create more efficacious products.

Relatively large amounts of the organoclay compositions are needed to impart the required viscosity in such systems, especially in those containing natural occurring oils. It is therefore an objective of this invention to provide an efficient thickener to impart the required viscosity to non-

aqueous coating systems, and in particular, to systems based on naturally occurring oils.

SUMMARY OF THE INVENTION

The instant invention is based on the unexpected discovery that an organophilic clay made in whole or in part with an organic cation containing ligands or moieties derived from a specific naturally occurring oil imparts a better viscosity to systems utilizing the same or similar natural oil as a solvent than is achieved by conventional organophilic clay gellants.

A new type of organophilic clay thickener has therefore been discovered which thickens coating systems comprised of or containing naturally occurring oils including vegetable oils. It has been unexpectedly discovered that these special organophilic clays are very efficient without affecting the other properties required from the system.

Thus, according to one aspect of the invention, an organophilic clay thickener is provided which comprises the reaction product of a smectite type clay and an organic cation containing a naturally occurring oil residue in an amount of from 75% to about 150% of the cation exchange capacity of the smectite type clay. Optionally, the organophilic clay may contain several such organic cations as well as cations of other types and in addition various anions. Such cations may contain aliphatic, aromatic or alkoxylated quaternary salts.

The present invention also contemplates a process for preparing an organophilic clay thickener for a naturally occurring oil which comprises:

- (a) preparing an aqueous slurry of a smectite-type clay;
- (b) adding to the slurry an organic cation derived from the same naturally occurring oil residue occurring in an amount of from about 75% to about 150% of the cation exchange capacity of the smectite-type clay; and optionally, other cation and/or an anion; and
- (c) reacting the resulting mixture for a sufficient time to form an organophilic clay gellant.

The first and other organic cations may be added to the clay slurry separately in any order or simultaneously.

The invention also provides non-aqueous solvent compositions thickened with the above-indicated organophilic clay thickeners.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As stated above, one aspect of the present invention relates to an improved, more efficient organophilic clay thickener for naturally occurring oil systems. The organophilic clay is prepared by reacting a smectite-type clay with an organic cation derived from a selected compatible naturally occurring oil residue, and optionally with other organic cations such as alkoxylated quaternary ammonium salts. The combination of a special designed compatible organoclay having a specific cation component, to match and thicken the naturally occurring fluid is believed to be unique.

While not wishing to be bound by any theory, it is believed that the naturally occurring oil residue which forms part of the organophilic clay after reaction renders the organophilic clay more compatible with the non-aqueous composition of the same general type, thus enabling the system to form a three dimensional network structure which in turn provides the composition with its enhanced rheological properties.

According to a first aspect of the invention, an organophilic clay thickener is provided which comprises the reac-

tion product of a smectite-type clay and an organic cation containing a naturally occurring oil residue in an amount of from about 75% to about 150% of the cation exchange capacity of the smectite-type clay.

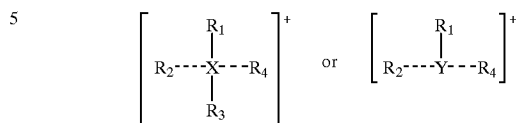
The preferred clay which is used in the present invention is a smectite-type clay having a cationic exchange capacity of at least 75 milliequivalents per 100 grams of clay as determined by the well-known ammonium acetate or methylene blue methods. Smectite-type clays are well known in the art and are commercially available from a variety of sources. Prior to use in the formulations of the instant invention, the clays are preferably converted to the sodium form if they are not already in this form. Smectite-type clays prepared synthetically may also be used to prepare the novel organic clay complexes of the invention.

Representative of smectite-type clays useful in accordance with the present invention are the following: montmorillonite, bentonite, beidellite, hectorite, saponite, stevensite, sauconite, nontronite and the like and mixtures thereof. Both processed and unprocessed clays can be used. The preferred clays used in the present invention are bentonite and hectorite.

In addition, smectite-type clays which have been subjected to the application of shear may also be used. To achieve shearing of the smectite-type clay, the clay is typically dispersed in water at a concentration of from about 0.5 to about 80% by weight. The slurry may optionally be first centrifuged to remove non-clay impurities which constitute about 10% to about 50% of the starting clay composition. Of course, if the clay has previously been treated, such as by the clay vendor, to remove the impurities, the treated clay can be formed into a slurry and subjected to shear conditions. Shear can be imparted to the smectite-type clay slurry by means of commercially available equipment that is known to impart high shear to the material. Representative processes for shearing smectite clay are described in U.S. Pat. Nos. 4,695,402 and 4,743,098.

The organic salts which are useful in this invention may be selected from a variety of materials that are capable of forming an organoclay by exchange of cations with the smectite-type clay. The organic cations which are reacted with the smectite-type clay have a positive charge localized on a single atom or on a small group of atoms within the compound. For example, the cation may be provided by a compound selected from the group consisting of quaternary ammonium salts, phosphonium salts, sulfonium salts and mixtures thereof. The organic cation should contain at least one residue of a naturally occurring oil. The remaining groups of the cation may be selected from the group consisting of (a) linear or branched aliphatic, alicyclic or aromatic groups having 1 to 22 carbon atoms; (b) aralkyl groups which are benzyl and substituted benzyl moieties including fused ring moieties having linear or branches 1 to 22 carbon atoms in the alkyl portion of the structure; (c) aryl groups such as phenyl and substituted phenyl including fused ring aromatic substituents; (d) beta, gamma-unsaturated groups having six or less carbon atoms or hydroxyalkyl groups having 2 to 6 carbon atoms; and (e) hydrogen. The naturally occurring oil residue may be derived from naturally occurring oils such as corn oil, coconut oil, soybean oil, cottonseed oil, castor oil, linseed oil, safflower oil, palm oil, peanut oil, tung oil and the like. The oil may be of natural sources or a synthetic version of same or modifications of a naturally occurring oil using known techniques.

The organic cation can be provided by a compound selected from the group consisting of at least one of the following formulae:



wherein X is nitrogen or phosphorous, Y is sulfur, R₁ is a linear or branched, saturated or unsaturated residue of a natural oil and R₂, R₃ and R₄ are independently selected from the group consisting of (a) linear or branched alkyl groups having 1 to 22 carbon atoms; (b) aralkyl groups which are benzyl and substituted benzyl moieties including fused ring moieties having linear chains or branches of 1 to 22 carbon atoms in the alkyl portion of the structure; (c) aryl groups such as phenyl and substituted phenyl including fused ring aromatic substituents; (d) beta, gamma unsaturated groups having six or less carbon atoms or hydroxyalkyl groups having 2 to 6 carbon atoms; and (e) hydrogen. It should be understood that R₂, R₃, or R₄ can also be the residues of natural oils in lieu of a) through e). U.S. Pat. No. 4,664,820 describes some of such organic salts.

The anion which will normally accompany the organic cation is typically one that will not adversely affect the reaction product. Such anions include, for example, chloride, bromide, iodide, hydroxyl, nitrite and acetate.

The preparation of the organic salt can be achieved by techniques well-known in the art. For example, when preparing a quaternary ammonium salt, one skilled in the art would prepare a dialkyl secondary amine, for example, by the hydrogenation of nitriles, and then form the methyl dialkyl tertiary amine by reductive alkylations using formaldehyde as a source of the methyl radical.

The other organic cations utilized in the products of the invention comprise quaternary salts which contain aliphatic, aromatic or alkoxy moieties.

Illustrative examples of suitable alkoxyated quaternary ammonium chloride compounds include those available under the tradename Ethoquad from Akzo Chemicals, namely, methyl bis(2-hydroxyethyl)cocoalkyl ammonium chloride, methyl bis(polyoxyethylene (15)) cocoalkyl quaternary ammonium chloride, methyl bis(2-hydroxyethyl) oleyl ammonium chloride, methyl bis(polyoxyethylene (15)) oleyl quaternary ammonium chloride, methyl bis(2-hydroxyethyl) octadecyl ammonium chloride, and methyl bis(polyoxyethylene (15)) octadecyl quaternary ammonium chloride.

The present invention also contemplates a process for preparing an organophilic clay thickener for a naturally occurring oil which comprises:

- (a) preparing an aqueous slurry of a smectite-type clay;
- (b) adding to said slurry an organic cation derived from a naturally occurring oil residue of the type of the naturally occurring oil to be thickened in an amount of from about 75% to about 150% of the cation exchange capacity of the smectite-type clay; and optionally, other organic cations and reacting the resulting mixture for a sufficient time to form an organophilic clay thickener.

The organoclays of this invention may be prepared by admixing the clay, organic salts and water together, preferably at temperatures within the range from 20° C. to 100° C., and most preferably from 35° C. to 80° C. for a period of time sufficient for the organic compounds to react with the clay. The reaction is followed by filtering, washing, drying

and grinding. The organic salts may be added simultaneously or at separate intervals.

The amount of organic salts added to the clay for purposes of this invention must be sufficient to impart to the clay the improved gelling and dispersion characteristics. This amount is defined as the milliequivalent ratio, which is the number of milliequivalents (m.e.) of the organic salt in the organoclay per 100 grams of clay, 100% active clay basis.

It should also be understood that a mixture of organic salts can be utilized including a mixture of a quaternary compatible with the system to be thickened with a quaternary which is not so compatible. For example a soya oil based ink can be thickened using an organoclay made with a soya based quaternary and a non soya based quaternary.

The organophilic clay gellants prepared according to this invention may be used as rheological additives in non-aqueous compositions such as inks, paints, varnishes, enamels, waxes, paint-varnish, oil base drilling fluids, lubricants and grease, polyesters, epoxy resins, adhesives, sealants, cosmetics, detergents, and the like. Consequently, the invention also provides non-aqueous solvent compositions thickened with the above-indicated organophilic clay thickener.

The organophilic clay complexes of the invention are added to the non-aqueous compositions in amounts sufficient to obtain the desired rheological properties. Amounts of the organophilic clay complexes in the non-aqueous compositions are from about 0.01% to 15%, preferably from about 0.3% to 5%, based on the total weight of the non-aqueous fluid system.

The following examples are given to illustrate the invention, but are not deemed to be limiting thereof.

EXAMPLE 1

This example illustrates the preparation of an organophilic clay gellant composition according to the present invention.

45.00 grams of dried bentonite clay, which has been previously treated in water by centrifugation to remove non-clay impurities and ion-exchanged to provide the clay in sodium form, is mixed with water to form a 3% by weight slurry of clay in water. The slurry is heated to 70° C. in a reaction flask of suitable size equipped with a stirrer, thermometer and addition funnel. 21.61 grams of trimethyl soya quaternary ammonium chloride (140 milliequivalents per 100 grams of clay solids) dissolved in 21.61 grams of isopropanol is added to the mixture. The mixture is stirred for 1 hour at 70° C. The product is filtered through a Buchner funnel to collect the solids. The wet solids are reslurried in 1500 grams of water at 70° C. for 20 minutes and then re-collected on a Buchner funnel. The filtercake is dried in a 60° C. oven for 16 hours.

COMPARATIVE EXAMPLE A

For comparative purposes, the procedure of Example 1 is repeated, except that dimethyl dihydrogenated tallow quaternary ammonium chloride is the organic salt used.

EXAMPLE 2

This Example illustrates the preparation of an organophilic clay gellant containing two types of organic salts according to the present invention.

45.00 grams of dried bentonite clay, which has been previously treated in water by centrifugation to remove non-clay impurities and ion-exchanged to provide the clay in sodium form, is mixed with water to make a 3% by weight

slurry of clay in water. The slurry is heated to 70° C. in a reaction flask of suitable size equipped with a stirrer, thermometer and addition funnel. 0.18 grams of methyl bis(2-hydroxyethyl) oleyl quaternary ammonium chloride (1 milliequivalent per 100 grams of clay solids), and 21.61 grams of trimethyl soya quaternary ammonium chloride (140 milliequivalents per 100 grams of clay solids) in 21.61 grams of isopropanol is added to the mixture. The mixture is stirred for 1 hour at 70° C. and then filtered through a Buchner funnel to collect the solids. The wet solids are reslurried in 1500 grams of water at 70° C. for 20 minutes and then re-collected on a Buchner funnel. The filtercake is dried at 60° C. in an oven for 16 hours.

EXAMPLE 3-5

These Examples demonstrate the dispersion and viscosity-build properties provided when the organophilic clay gellants are used in a soya bean oil based ink formulation. A red soya news ink formulation is prepared according to Formulation 1.

FORMULATION 1

Soya News Red Ink Formula			
Ingredient	Generic Name	Manufacturer	Formulation (parts by wt.)
LR 6247 SB Lithol Rubine	Flushed Color	Magruder Color	26.25
Special T Blown Soya Oil	Oxidized Soya Bean Oil	Spencer-Kellogg Div. Reichhold Chemicals	40.27
Mix at 8000 rpm until uniform, then add:			
Polar Activator	Propylene Carbonate/ Water		0.76
Rheological Additive			3.78
Disperse at 8000 rpm for 20 minutes, then add as letdown:			
Superior Soya Oil	Highly Refined Soybean Oil A	Spencer-Kellogg Div. Reichhold Chemicals	28.94
Total			100.00

A red ink is prepared according to Formulation 1. The ink is allowed to equilibrate at room temperature for 24 hours. Tack and misting are measured with a Thwing-Albert Inkometer operating at 1200 rpm and 90° F. Tack is measured according to ASTM Method D4361-84 entitled "Apparent Tack of Printing Inks by the Inkometer."

NPRI (National Printing Ink Research Institute) grind values are measured to evaluate dispersion according to ASTM Method D1316-68 entitled "Fineness of Grind of Printing Inks by the Production Grindometer." Viscosity for the ink formulations are determined using a Brookfield RVT Viscometer with a No. 15 spindle. Dispersion measurements, Brookfield viscosities, tack, and misting are presented in Table 1.

The high efficiency of the organophilic clay of the invention is demonstrated in FIG. 1. The graph shows viscosity profiles (viscosity as a function of shear rate) of two soya bean oil based inks. It is obvious that the efficiency of the ink containing the organophilic clay of the invention (example 1) is superior to that exhibited by an ink system containing the same amount of comparative example A. FIG. 2 shows the recovery of viscosity after shearing the ink at high shear rates. In this experiment, an ink composition according to

Formulation 1 is sheared at a shear rate of 184 1/S for 180 seconds and then the increase in viscosity is monitored at a shear rate of 0.184 1/S as a function of time. The test is performed using a Bohlin VOR Rheometer (Bohlin Instruments, Cranbury, N.J.).

TABLE 1

Ex.	Organic salt	Grind	Tack	Misting	Brookfield Visc.	
					20 rpm	2.5 rpm
3	trimethyl soya ^a	0/18 M	6.4	F	14375	17500
4	trimethyl soya/ methyl bis(2- hydroxyethyl)oleyl ^b	0/07 LM	6.7	F	13125	16000
5	dimethyl dihydrogenated tallow ^c	0/1 LM	5.5	F	5125	11500

M = Medium; LM: = Light Medium; F = Fair
^aexample 1; ^bexample 2; ^ccomparative example A

EXAMPLE 6

This Example illustrates the preparation of an organophilic clay gellant containing an organic cation and an organic anion.

45.00 grams of dried bentonite clay, which has been previously treated in water by centrifugation to remove non-clay impurities and ion-exchanged to provide the clay in sodium form, is mixed with water to make a 3% by weight slurry of clay in water. The slurry is heated to 70° C. in a reaction flask of suitable size equipped with a stirrer, thermometer and addition funnel. 1.72 grams of sodium stearate (12.5 milliequivalents per 100 grams of solids) in 50 grams water and 21.61 grams of trimethyl soya quaternary ammonium chloride (140 milliequivalents per 100 grams of clay solids) is added to the mixture. The mixture is stirred for 1 hour at 70° C. and then filtered through a Buchner funnel to collect the solids. The wet solids are reslurried in 1500 grams of water at 70° C. for 20 minutes and then re-collected on a Buchner funnel. The filtercake is dried at 60° C. in an oven for 16 hours.

EXAMPLES 7–14

These examples illustrate the effect of drying conditions on the properties provided when the organophilic clay gellants in Example 1 and Comparative Example A are used in a soya bean oil based ink formulation. Dispersion measurements, Brookfield viscosity, tack and misting are presented in Table 2.

TABLE 2

Ex.	Drying Method	Tem- perature	Grind	Tack	Mist- ing	Brookfield Visc.	
						20 rpm	2.5 rpm
7 (a)	Forced air oven	65° C.	0/16 M	6.7	F	15000	18500
8 (b)	Forced air oven	65° C.	0/10 M	5.7	F	5312	13000
9 (a)	Forced air oven	85° C.	0/18 MH	6.3	F	13500	16500
10 (b)	Forced air oven	85° C.	0/24 MN	5.3	F	5375	12500
11 (a)	Fluid bed dryer	65° C.	0/18 M	6.4	F	14375	17500

TABLE 2-continued

Ex.	Drying Method	Tem- perature	Grind	Tack	Mist- ing	Brookfield Visc.	
						20 rpm	2.5 rpm
12 (b)	Fluid bed dryer	65° C.	0/10 LM	5.5	F	5125	11500
13 (a)	Fluid bed dryer	93° C.	0/12 M	6.5	F	12875	15000
14 (b)	Fluid bed dryer	93° C.	0/06 LM	5.8	F	5125	11000

(a) Example 1; (b) Comparative Example A
M = Medium H = Heavy L = Light F = Fair

EXAMPLES 15–20

These examples illustrate the effect of the amount of the organic cation in the organophilic clay on the properties provided when the organophilic clay gellant is used in a soybean oil based ink formulation. Dispersion, Brookfield viscosity, tack and misting are presented in Table 3. The preparation of the organophilic is given in Example 1.

TABLE 3

Ex.	Meq/100 Clay	Grind	Tack	Misting	Brookfield Visc.	
					20 rpm	2.5 rpm
15	100	0/30 H	6.2	F	4750	5500
16	110	0/29 MH	6.5	F	9875	11500
17	120	0/29 M	6.4	F	20500	29500
18	130	0/27 LM	6.6	F	15250	20000
19	140	0/18 M	6.4	F	14375	17500
20	150	0/18 M	6.4	F	10250	13000

H = Heavy M = Medium L = Light F = Fair

EXAMPLES 21–23

These examples illustrate the effect of the organic anion in the organophilic clay on the properties provided when the organophilic clay gellant is used in a soybean oil based ink formulation. Dispersion, Brookfield viscosity, tack and misting are presented in Table 4. The preparation of the organophilic clay is given in Example 6.

TABLE 4

Ex.	Organic Anion	Grind	Tack	Misting	Brookfield Visc.	
					20 rpm	2.5 rpm
19	none	0/18 M	6.4	F	14375	17500
21	stearate	0/08 LM	6.8	F	14500	16500
22	succinate	0/24 LM	5.7	F	8125	9000
23	palmitate	0/12 LM	5.7	F	10500	12000

Based on the results, it is apparent that the organophilic clay compositions provided by the invention are highly effective in improving the rheological properties of non-aqueous systems.

The invention thus being described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the claims.

What is claimed is:

1. An organophilic clay thickener for soya oil systems comprising the reaction production of:

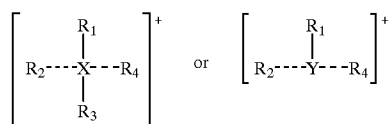
(a) a smectite-type clay; and

(b) an organic cation derived from a soya oil residue in an amount of from about 75% to about 150% of the cation exchange capacity of the smectite-type clay.

2. The organophilic clay thickener of claim 1, wherein said smectite type clay is selected from the group consisting of montmorillonite, bentonite, beidellite, hectorite, saponite, stevensite, sauconite and nontronite and mixtures thereof.

3. The organophilic clay thickener of claim 1, wherein said organic cation is provided by a compound selected from the group consisting of quaternary ammonium salts, phosphonium salts, sulfonium salts, and mixtures thereof.

4. The organophilic clay thickener of claim 1, wherein said organic cation is provided by a compound selected from the group consisting of:



wherein X is nitrogen or phosphorous, Y is sulfur, R₁ is a residue of a soya oil and R₂, R₃ and R₄ are independently selected from the group consisting of (a) linear or branched alkyl groups having 1 to 22 carbon atoms; (b) aralkyl groups which are benzyl and substituted benzyl moieties including fused ring moieties having linear chains or branches of 1 to 22 carbon atoms in the alkyl portion of the structure; (c) aryl groups; (d) beta, gamma unsaturated groups having six or less carbon atoms or hydroxyalkyl groups having 2 to 6 carbon atoms; and (e) hydrogen; wherein R₂, R₃ and R₄ may also be residues of naturally occurring soya oil in lieu of (a) to (e).

5. The organophilic clay thickener of claim 1 further comprising an organic anion.

6. The organophilic clay thickener of claim 5, wherein said organic anion is provided by a compound selected from the group consisting of stearic acid, palmitic acid, succinic acid, their corresponding salts and mixtures thereof.

7. The organophilic clay thickener of claim 1 including a second organic cation wherein said second organic cation is derived from aliphatic, aromatic or alkoxylated groups.

8. A process for preparing an organophilic clay thickener for soya oil systems which comprises:

(a) preparing an aqueous slurry of a smectite-type clay;

(b) adding to said slurry an organic cation derived from a soya oil residue in an amount of about 75% to about 150% of the cation exchange capacity of the smectite-type clay and;

(c) reacting the resulting mixture for a sufficient time to form an organophilic clay.

9. A non-aqueous fluid system which comprises:

(a) a soya oil composition and

(b) an organophilic clay thickener comprising the reaction product of a smectite-type clay and an organic cation derived from a soya oil residue in an amount from about 75% to about 150% of the cation exchange capacity of the smectite-type clay.

10. The non-aqueous fluid system of claim 9, wherein said non-aqueous composition is selected from the group consisting of inks, paints, varnishes, enamels, waxes, paint-varnish, lacquer remover, oil base drilling fluids, lubricating grease, polyesters, epoxy resins, adhesives, sealants, cosmetics and detergents.

* * * * *



US005292908A

United States Patent [19]

Onikata et al.

[11] Patent Number: 5,292,908

[45] Date of Patent: Mar. 8, 1994

[54] MODIFIED BENTONITE

[75] Inventors: Masanobu Onikata, Gunma; Mitsuji Kondo, Tochigi, both of Japan

[73] Assignee: Hojun Kogyo Co., Ltd., Annaka, Japan

[21] Appl. No.: 3,049

[22] Filed: Jan. 11, 1993

[30] Foreign Application Priority Data

Mar. 9, 1992 [JP] Japan 4-85055

[51] Int. Cl.⁵ C07F 5/06

[52] U.S. Cl. 556/173

[58] Field of Search 556/173

[56] References Cited

U.S. PATENT DOCUMENTS

2,531,427 11/1950 Hauser 260/448
4,287,086 9/1981 Finlayson et al. 556/173 X

4,402,881 9/1983 Alther 556/173
4,407,728 10/1983 Ball et al. 556/173 X
4,469,639 9/1984 Thompson et al. 556/173 X
4,474,705 1/1984 Clay et al. 556/173
4,474,706 10/1984 Clay et al. 556/173
4,528,038 7/1985 Williams 556/173 X
4,874,728 10/1989 Elliott et al. 501/148
5,110,501 5/1992 Knudson et al. 556/173 X

FOREIGN PATENT DOCUMENTS

33-3018 4/1958 Japan .
57-111371 7/1982 Japan .

Primary Examiner—Paul F. Shaver
Attorney, Agent, or Firm—Kenyon & Kenyon

[57] ABSTRACT

Modified bentonite is disclosed, comprising modified bentonite which can be dispersed in water to perform a function of adjusting rheology of an aqueous liquid.

3 Claims, No Drawings

MODIFIED BENTONITE

FIELD OF THE INVENTION

This invention relates to surface-modified bentonite which is dispersible in water or organic liquids to exhibit an excellent function of adjusting rheology.

BACKGROUND OF THE INVENTION

Bentonite deposit has a complicated composition mainly formed of smectites and containing free silica minerals, such as quartz, α -cristobalite, and opal; silicate minerals, such as feldspar, mica, and zeolite; carbonates or sulfates of alkaline earth metals, such as calcite, dolomite, and gypsum; and, in addition, iron compounds and humus. Since bentonite ore mined from bentonite deposit usually has a water content of 15 to 35%, it is primarily broken and dried in the sun or hot air to obtain bentonite ore having a water content of 5 to 10%. The dried bentonite ore is pulverized by means of an attrition grinding machine, such as a centrifugal roller mill, or an impact mill, such as a hammer mill. The resulting bentonite powder is widely used in various industrial fields, for example, as a binder for foundry sand, a main ingredient for a drilling fluid used in oil well drilling, geothermal well drilling, or hot spring boring, or a main agent of a stabilizing liquid used in continuous diaphragm wall construction or earth drilling in engineering works. As stated above, bentonite for these uses basically has a composition based on the natural bentonite deposit, containing much non-clay substances.

On the other hand, liquid fine chemicals widely used in various industrial fields, such as coatings, printing inks, and cosmetics, contain various natural or chemical substances for rheological adjustment. Purified bentonite powder, which is obtained by dispersing bentonite in water, removing unfavorable non-clay substances by spontaneous sedimentation or centrifugal separation, and drying the resulting purified bentonite sol by evaporation, is used as a rheological adjuster for aqueous coatings, aqueous emulsions, or the like aqueous colloidal dispersion products.

Because the bentonite powder which is merely purified can not be dispersed in organic-solvents, it is not suitable as a rheological adjuster for liquid products containing an organic solvent, such as alkyd resin coatings or other synthetic resin coatings, printing inks, and sealants. Hence, the purified bentonite is rendered organophilic by combining with a quaternary ammonium cation (see U.S. Pat. No. 2,531,427), a composite of a quaternary ammonium cation and a nonionic organic compound (see Japanese Patent 244306 corresponding to JP-B-3018 (The term "JP-B" as used herein means an examined Japanese patent publication), or a combination of a quaternary ammonium cation and an organic anion (see JP-A-57-111371), (the term "JP-A" as used herein means an "unexamined published Japanese patent applications") to be used as a rheological adjuster which can be dispersed in organic liquids.

However, the above-mentioned purified bentonite or organophilic modified bentonite has disadvantages as described below.

Purified bentonite exhibits unique rheological characteristics which differ from that of organic (high) polymers, e.g., carboxymethyl cellulose, poly(sodium acrylate), and polyacrylamide. However, because its function in increasing viscosity is generally insufficient, it

must be added in a considerable proportion to obtain a sufficient effect in increasing viscosity, which leads to generation of various undesired side effects, such as impairment of the color tone of products. Accordingly, the amount of the purified bentonite incorporated is limited.

Organophilic modified bentonite has insufficient dispersibility in a solvent system comprising hydrocarbons only, and it is necessary to add to the dispersion system an adequate amount of a highly polar organic compound having a low molecular weight, such as methanol, ethanol, or acetone, to obtain organophilic modified bentonite which is sufficiently dispersed. However, such usage is not only complicated but involves a problem that an unfavorable polar compound should be introduced into the system.

SUMMARY OF THE INVENTION

An object of the present invention is to provide modified bentonite which can be dispersed in an aqueous system to provide an excellent effect in increasing viscosity which has not been achieved with conventional purified bentonite products.

Another object of the present invention is to provide organophilic modified bentonite which can easily be dispersed in a hydrocarbon solvent system to provide an excellent effect in increasing viscosity without use of a highly polar organic compound.

The inventors have found that the above objects of the present invention are accomplished by purified bentonite treated with an alkyltrialkoxysilane.

The present invention relates to modified bentonite which can be dispersed in water to perform a function of adjusting rheology of an aqueous liquid, which is obtained by

adding at least one alkyltrialkoxysilane represented by formula (I):



wherein R^1 represents a saturated alkyl group having from 1 to 22 carbon atoms; and R^2 represents a methyl group, an ethyl group, a propyl group or a butyl group, to bentonite in such an amount that the resulting product can retain an excellent water-dispersibility, and then stirring and grinding the mixture in a water-free atmosphere to add an alkylsilyl group to a part of the surface of bentonite particles.

The present invention also relates to modified bentonite which can be easily dispersed in an organic liquid to perform a function of adjusting rheology of an organic liquid, which is obtained by adding to bentonite (1) from 1 to 1.5 equivalent of a quaternary ammonium cation represented by formula (II):



wherein R^3 represents a long-chain alkyl group having from 12 to 22 carbon atoms; R^4 represents a methyl group, a benzyl group or a long-chain alkyl group having from 12 to 22 carbon atoms; and R^5 represents a methyl group, based on the cation exchange capacity of said bentonite and (2) from 0.5 to 15 parts by weight of at least one alkyltrialkoxysilane represented by formula (I):



wherein R^1 and R^2 each has the same meaning as defined above, per 100 parts by weight of said bentonite to render said bentonite hydrophobic.

DETAILED DESCRIPTION OF THE INVENTION

Bentonite which can be used as a raw material in the present invention is substantially water-free purified bentonite which is obtained by removing non-clay substances from a crude bentonite suspension using spontaneous sedimentation or centrifugal separation to recover a purified bentonite sol, evaporating the resulting purified bentonite sol, and finally drying at a temperature of from 150 to 200° C.

The modified bentonite which can provide an excellent effect in increasing viscosity in an aqueous dispersion system according to the present invention can be prepared by adding to purified bentonite in a water-free atmosphere an alkyltrialkoxysilane of the above formula in such an amount that does not cause the resulting product to exhibit water repellency, and, after stirring, grinding the mixture to thereby add an alkylsilyl group to a part of the surface of bentonite particles.

Specific examples of the alkyltrialkoxysilane represented by formula (I) which can be used in the present invention include methyltrimethoxysilane, methyltriethoxysilane, propyltrimethoxysilane, butyltrimethoxysilane, hexyltrimethoxysilane, octyltriethoxysilane, dodecyltriethoxysilane, and octadecyltriethoxysilane. Among these, hexyltrimethoxysilane, octyltriethoxysilane, dodecyltriethoxysilane, and octadecyltriethoxysilane are preferred.

The amount of the alkyltrialkoxysilane to be added to purified bentonite is experimentally decided from the degree of non-water repellency, wetting with water, and waterdispersibility of the finally obtained modified bentonite. In most cases, while not limiting, such an amount ranges generally from 0.5 to 15 parts by weight, preferably from 1 to 10 parts by weight, and most preferably from 1 to 7 parts by weight, per 100 parts by weight of bentonite.

By the treatment with the alkyltrialkoxysilane, an alkylsilyl group is added to hydrophilic hydroxyl groups present on the surface of bentonite particles, such as a silanol group, to render the part of the bentonite surface hydrophobic. The thus modified bentonite particles, when dispersed in an aqueous system, form a plastic structure due to association of the hydrophobic groups thereof and, as a result, considerably increase the apparent viscosity of the aqueous system and endow the aqueous system with favorable thixotropic properties.

The organophilic modified bentonite containing an alkylsilyl group for organic liquids, particularly hydrocarbon solvent systems, according to the present invention is preferably prepared by dissolving an alkyltrialkoxysilane in a quaternary ammonium cation solution, immediately adding the solution to a purified bentonite sol to conduct a reaction, followed by dehydration, drying, and pulverizing. The organophilic modified bentonite may also be prepared by re-dispersing in water the abovementioned alkyltrialkoxysilane-treated bentonite produced in a water-free atmosphere and then adding thereto a quaternary ammonium cation. However, the latter method is not practical because it requires re-dehydration and re-pulverizing, thus increasing cost.

Specific examples of the alkyltrialkoxysilane which can be used in the preparation of the organophilic modified bentonite are the same as those enumerated above.

The amount of the alkyltrialkoxysilane added ranges from 0.5 to 15 parts by weight per 100 parts by weight of bentonite.

The quaternary ammonium cation represented by formula (II) shown above which can be used in the present invention can be added in the form of a quaternary ammonium chloride. The amount of the quaternary ammonium cation added (i.e., the amount of the quaternary ammonium cation added) ranges from 1 to 1.5 equivalent and preferably from 1 to 1.25 equivalent, based on the cation exchange capacity of the starting bentonite.

By the above-mentioned treatment with the quaternary ammonium cation and alkyltrialkoxysilane, the alkyltrialkoxysilane is solubilized by a quaternary ammonium salt having surface activity and, at the same time, undergoes partial hydrolysis to form an alkylsilyl polymer, which is added to the hydrophilic sites on the surface of bentonite particles together with the quaternary ammonium cation to thereby accomplish a treatment for rendering the bentonite surface hydrophobic to such a degree that a quaternary ammonium cation alone cannot achieve. The resulting modified bentonite particles are easily dispersed in a hydrocarbon organic liquid to form a plastic structure due to association of the hydrophobic particles, with which a high apparent viscosity and favorable thixotropic properties can be imparted to the organic liquid system.

Bentonite which can be used in the present invention belongs to phyllosilicate minerals having a dioctahedral structure and/or a trioctahedral structure and having substantially a cation exchange capacity, which are selected from the group consisting of montmorillonite, beidellite, nontronite, hectorite and saponite, and further the bentonite may be artificial phyllosilicates.

The present invention is now illustrated in greater detail with reference to Examples, but it should be understood that the present invention is not deemed to be limited thereto. All the percents and parts are by weight unless otherwise indicated.

EXAMPLE 1

One kilogram of bentonite produced in Wyoming, U.S.A. was poured into 50 kg of deionized water and allowed to stand overnight to be swollen. Then the mixture was dispersed in a disper for 1 hour, and the resulting bentonite suspension was centrifuged at 4,000 rpm for 10 minutes to recover 43.5 kg of the supernatant purified bentonite sol (solids content: 1.03%). The purified bentonite sol was dried in a hot air circulator at 100° C. to obtain flaky purified bentonite having a water content of 6%. The flaky purified bentonite was ground in Bantam Mill (manufactured by Hosokawa K.K.) to a size of 250 mesh and dried at 200° C. for 2 hours to obtain 425 g of water-free bentonite.

Fifty grams of the water-free bentonite were put in a 1000 ml-volume ceramic pot mill, and 1 g of alkyltrialkoxysilane shown in Table 1 below each was added thereto. After sealing, the mill was rotated for 30 minutes to prepare alkyltrialkoxysilane-modified bentonite (Samples 1 to 8).

Each of Samples 1 to 8 and the non-treated purified bentonite as prepared above was dispersed with water in a Hamilton Beach Mixer (manufactured by Hamilton Beach Inc.), and the rheological characteristics of the

aqueous dispersion solution were measured with a Fann Viscometer (Model 35 SA" manufactured by Fann Instrument Corp.) at 23° C. Thixotropy was expressed in terms of a ratio of apparent viscosity at 300 rpm (V_{300}) to apparent viscosity at 600 rpm (V_{600}) (i.e., V_{300}/V_{600}). The results obtained are shown in Table 1.

ples 201 and 202). The cation exchange capacity of the purified bentonite was 72 milliequivalents per 100 g. The quaternary ammonium cation was added in an amount of 83 milliequivalents per 100 g of bentonite (i.e., water-free bentonite).

Samples 201 and 202 were compared with various commercially available organophilic modified benton-

TABLE 1

Sample No.	Silane Treating Agent	Concentration (part*)	Apparent Viscosity		Plastic Viscosity (cps)	Yield Value (lb/1000 ft ²)	Thixotropy V_{300}/V_{600}
			V_{300} (cps)	V_{600} (cps)			
Purified bentonite (non-treated)		2	3.5	3.0	2.5	1.0	1.17
		3	6.5	5.5	4.5	2.0	1.18
		5	33.0	23.8	14.5	18.5	1.39
Commercially available purified bentonite ("Kunipia G" produced by Kunimine Kogyo K.K.)		1	3.0	2.5	2.0	1.0	1.20
		2	6.0	5.3	4.5	1.5	1.13
		3	16.0	13.8	11.5	4.5	1.16
Sample 1 methyltrimethoxysilane		2	9.0	7.0	5.0	4.0	1.29
		3	33.5	22.5	11.5	22.0	1.49
		5	74.0	55.3	36.5	37.5	1.34
Sample 2 methyltriethoxysilane		2	8.5	6.8	5.0	3.5	1.25
		3	17.0	12.8	8.5	8.5	1.33
		5	70.0	55.0	40.0	30.0	1.27
Sample 3 propyltrimethoxysilane		2	8.5	6.3	4.0	4.5	1.35
		3	24.5	16.0	7.5	17.0	1.53
Sample 4 butyltrimethoxysilane		2	14.0	9.5	5.0	9.0	1.47
		3	42.0	24.0	6.0	36.0	1.75
Sample 5 hexyltrimethoxysilane		1	6.5	4.8	3.0	3.5	1.35
		2	38.5	22.0	5.5	33.0	1.75
		3	105.0	57.8	10.5	94.5	1.82
Sample 6 octyltriethoxysilane		1	5.0	3.8	2.5	2.5	1.32
		2	31.5	19.0	6.5	25.0	1.66
		3	83.5	46.8	10.0	73.5	1.78
Sample 7 dodecyltriethoxysilane		1	7.0	5.0	3.0	4.0	1.40
		2	40.0	23.3	6.5	33.5	1.72
		3	123.0	67.5	12.0	111.0	1.82
Sample 8 octadecyltriethoxysilane		1	6.5	5.0	3.5	3.0	1.30
		2	29.5	18.0	6.5	23.0	1.64
		3	82.5	44.5	6.5	76.0	1.85

Note:

*Part by weight per 100 parts by weight of water

As is apparent from the results of Table 1, the aqueous dispersion solutions of Samples 1 to 8 are markedly superior to the non-treated purified bentonite or the commercially available purified bentonite in apparent viscosity, yield value, and thixotropy, and further the alkyltrialkoxysilane-modified bentonite according to the present invention exhibits an excellent function in rheological adjustment of an aqueous liquid system.

EXAMPLE 2

In 20 kg of deionized water was poured 400 g of bentonite produced in Wyoming, U.S.A. and allowed to stand overnight to be swollen. The mixture was dispersed with a disper for 1 hour. The resulting bentonite suspension was allowed to stand for 3 days to sediment non-clay substances. The purified bentonite sol (16 kg; solids content: 1.39%) of the upper phase was obtained by decantation.

In a 5000 ml-volume stainless steel beaker was put 1,440 g of the purified bentonite sol (corresponding to 20 g of water-free bentonite) and heated to 60° C. while stirring with a disper. Separately, 7.0 g of dimethyloctadecylbenzylammonium chloride was dissolved in 70 ml of deionized water at 60° C., and 2.0 parts of octadecyltriethoxysilane or methyltrimethoxysilane per 100 parts of bentonite was further dissolved therein by stirring. The solution was added to the bentonite sol, and the mixture was stirred for 30 minutes, followed by filtration. The filter cake was washed with water, dehydrated, dried to a water content of 5%, and ground in Bantam Mill (manufactured by Hosokawa K.K.) (Sam-

ple products shown in Table 2 below in terms of swellability in toluene and rheological characteristics when dispersed in toluene. The swellability was measured by putting 100 ml of toluene in a measuring cylinder, adding 2.0 g of a test sample, and measuring the total volume after 24 hours at 20° C. The viscosity was measured by dispersing 3.0 g of a test sample in 150 g of toluene in a homogenizer at 10,000 rpm for 2 minutes and immediately measuring the apparent viscosity at 6 rpm or 60 rpm (V_6 or V_{60}) at 20° C. with a BL type viscometer. The thixotropy was expressed in terms of a V_6/V_{60} ratio. The results obtained are shown in Table 2.

TABLE 2

Sample	Silane Treating Agent (part*)	Swella-bility (ml/2 g)	Apparent Viscosity		Thixotropy (V_6/V_{60})
			V_6 (cps)	V_{60} (cps)	
Sample 201	octadecyltriethoxysilane (2.0)	47	580	96	6.40
Sample 202	methyltrimethoxysilane (2.0)	48	850	168	5.06
BENTONE SD-1*2	—	38	120	22	5.45
BENTONE SD-2*2	—	45	188	21	8.95
BENTONE SD-3*2	—	27	108	19	5.68
BENTONE 27*2	—	20	70	17	4.12
BENTONE 34*2	—	40	150	36	4.17

TABLE 2-continued

Sample	Silane Treating Agent (part* ¹)	Swella- bility (ml/2 g)	Apparent Viscosity		Thixotropy (V ₆ /V ₆₀)
			V ₆ (cps)	V ₆₀ (cps)	
BENTONE 38* ²	—	31	150	33	4.55
BENTONE 500* ²	—	32	200	36	5.56
NEW D ORBEN* ³	—	32	120	22	5.45
TIXOGEL VZ* ⁴	—	37	155	36	4.31
S BEN* ⁵	—	22	80	23	3.48
ORGANITE T* ⁵	—	29	95	28	3.39
ORGANITE* ⁵	—	32	205	52	3.94

Note:

*¹Part by weight per 100 parts by weight of bentonite (i.e. water-free bentonite).*²Trade name of the product of Rheox Inc., U.S.A.*³Trade name of the product of Shiraishi Kogyo K.K.*⁴Trade name of the product of Süd-Chemie AG, German.*⁵Trade name of the product of Nihon Yuki Nendo K.K.

Note: *1: Part by weight per 100 parts by weight of bentonite (i.e. water-free bentonite).

*2: Trade name of the product of Rheox Inc., U.S.A.

*3: Trade name of the product of Shiraishi Kogyo K.K.

*4: Trade name of the product of Süd-Chemie AG, German.

*5: Trade name of the product of Nihon Yuki Nendo K.K.

As is apparent from the results of Table 2, the alkyltrialkoxysilane-modified bentonite according to the present invention has a higher swellability, a higher apparent viscosity, and sufficient thixotropic properties in toluene alone as compared with any of the commercially (conventionally) available organophilic modified bentonite products and therefore performs excellent functions in adjustment of rheology of a hydrocarbon solvent system.

As described and demonstrated above, the present invention provides modified bentonite which is obtained by treating bentonite with an alkyltrialkoxysilane to make a part of the surface thereof hydrophobic without causing water repellency and which, when dispersed in an aqueous liquid, considerably increases the

apparent viscosity of the aqueous liquid to perform excellent rheology adjusting functions.

The present invention further provides organophilic modified bentonite which is obtained by treating bentonite with a quaternary ammonium cation and an alkyltrialkoxysilane and which exhibits excellent dispersibility in a hydrocarbon solvent system, such as toluene, to perform excellent functions in adjusting rheology of such a system.

The modified bentonite according to the present invention satisfies the demand of rheological adjustment essential to various industrial liquid products, either aqueous or organic, such as coatings, printing inks, ceramic slurries, sealants, and cosmetics.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. Modified bentonite which can be dispersed in water to perform a function of adjusting rheology of an aqueous liquid, which is obtained by adding at least one alkyltrialkoxysilane represented by formula (I):



wherein R¹ represents a saturated alkyl group having from 1 to 22 carbon atoms; and R represents a methyl group, an ethyl group, a propyl group or a butyl group, to bentonite in such an amount that the resulting product can retain an excellent water-dispersibility, and then stirring and pulverizing the mixture in a water-free atmosphere to add an alkylsilyl group to a part of the surface of bentonite particles.

2. Modified bentonite as claimed in claim 1, wherein said bentonite is purified water-free bentonite prepared by removing non-clay substances from a bentonite aqueous suspension using spontaneous sedimentation or centrifugal separation and drying the resulting purified bentonite sol.

3. Modified bentonite as claimed in claim 1, wherein said alkyltrialkoxysilane is used in an amount of from 0.5 to 15 parts by weight per 100 parts by weight of bentonite.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,292,908

DATED : March 8, 1994

INVENTOR(S) : Masanobu Onikata, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 7, lines 22-30 Delete entirely.

Column 8, line 29, change "R" to --R² --.

Signed and Sealed this

Twenty-third Day of August, 1994

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks