

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
RAD: 14-199043- -6	FECHA: 2016-06-16 13:26:34
DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 378 FASE NACIONAL INCLUIDO CAPITULO I
TRA: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II	FOLIOS: 10
ACT: 519 TRASLADOINFORME	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
ALICIA LLOREDA RICAURTE

Asunto: Radicación: 14-199043- -6
Trámite: 11
Evento: 378
Actuación: 519
Oficio: 7267
Folios: 10

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional					
Vía PCT (Fase Nacional)	X	Capítulo I	X	Capítulo II	
No. Solicitud Internacional	PCT/EP2013/055895				
Fecha de Presentación Internacional	21/03/2013				

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

1. Documentos estudiados

Descripción:	Radicado N° 14-199043-00000-0000	09/Septiembre/2014
Reivindicaciones:	Radicado N° 14-199043-00000-0000	09/Septiembre/2014
	Radicado N° 14-199043-00002-0000	06/Noviembre/2014
	Radicado N° 14-199043-00005-0000	23/Febrero/2016
Prioridades:	EP 12161144.6	23/Marzo/2012
	US 61/617,721	30/Marzo/2012

2. Análisis de la Prioridad

Se acepta la reivindicación de prioridad porque ésta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del capítulo primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por la solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. En el presente caso se estudiarán las reivindicaciones 1 a 25 del capítulo reivindicatorio (Radicado N°. 14-199043-00005-0000).

Título de la solicitud: “PREPARACIÓN DE PIGMENTOS”.

El problema planteado en esta solicitud consiste en la necesidad de proporcionar composiciones acuosas que contienen carbonato de calcio, alternativas, que proporcionan un mejor funcionamiento que las composiciones acuosas que contienen carbonato de calcio, existentes y que mejoren efectivamente las propiedades mecánicas y ópticas de un producto de papel recubierto con tal composición (Radicado N°. 14-199043-00000-0000, Pág. 9, Párr. 2).

Para resolver este problema técnico la solicitud en estudio proporciona una composición acuosa que contiene carbonato de calcio y métodos para la producción de tales composiciones acuosas que contienen el carbonato de calcio (Radicado N°. 14-199043-00000-0000, Pág. 5, Párr. 1).

El objeto de la presente solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C09C1/02, D21H17/00.

4. De la solicitud de patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

- Las reivindicaciones 1 – 7 y 12 – 15, no son concisas porque el término: “*al menos*”, es impreciso, por lo cual no permite distinguir la invención del estado de la técnica. Se sugiere sustituirlo por un término preciso o un rango concreto.
- Las reivindicaciones 2 – 4, 6 – 7, 9 – 19, 23 y 24, no son concisas porque las expresiones: “*preferentemente*”, “*más preferentemente*”, “*tales como*”, “*en especial*” precediendo una característica no son limitativas, y convierten la característica en opcional lo que no permite limitar el alcance de la reivindicación. Se sugiere incluir las características opcionales o preferentes en una reivindicación dependiente.
- Las reivindicaciones 1, 13, 15 -16, 19 y 23, hacen referencia a una composición acuosa que contiene carbonato de calcio y su método de producción. Sin embargo, las expresiones “*sal de un catión divalente o trivalente*”, “*sales de dialil dialquil amonio*” y “*polietileno iminas*”, abarcan un número indeterminado de compuestos que a su vez dan origen a un elevado número de composiciones de las cuales no se observa sustento en la descripción en cuanto a su preparación o efecto técnico. Se sugiere que el solicitante elimine del capítulo reivindicatorio cada una de las expresiones antes mencionadas y las reemplace por el nombre químico específico de los compuestos que fueron empleados en los ensayos realizados con la composición que se pretende reclamar.
- Las reivindicaciones 1, 3 – 5, 18 – 19 y 25, no son claras, ya que se caracteriza a la composición mediante la viscosidad de Brookfield, y al polímero en forma de peine mediante viscosidad y carga específica, que son resultados a alcanzar, que no definen la composición ni el polímero, puesto que las reivindicaciones incluirían no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado. Se sugiere reemplazarlos por las características

esenciales, estructurales o funcionales, que contribuyen a la obtención de ese efecto.

- Las reivindicaciones 1, 12 y 19 no son concisas porque el término “*agente de aglutinación*” no especifica un compuesto por su nombre químico o fórmula, sino por la función que desempeña. Se requiere definirlo por su nombre o estructura química.
- Las reivindicaciones 5 y 6 no son concisas. Las definiciones de los sustituyentes R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, X, Y, Z, m, n, o, a, b, c, d, R, R', α, β, abarcan un número indeterminado de compuestos que a su vez dan origen a un elevado número de formulaciones, de las cuales no se observa sustento en la descripción, para toda esa generalidad, en cuanto a su preparación o efecto técnico. Se sugiere restringir la solicitud a una razonable generalización del tipo de compuestos que ha sido probado, es decir, que se encuentran debidamente sustentados, por ejemplo, según lo mostrado en la siguiente tabla:

Sustituciones	Soporte de los ejemplos presentados
R	Metacrilato
R'	H, metilo
α	16, 113
β	48, 0

En este sentido, es importante señalar que si bien es cierto que una invención no está limitada por los ejemplos allí ilustrados, el capítulo reivindicatorio actualmente presentado corresponde a una generalización de carácter especulativo, que además involucra una extrapolación a un elevado número de compuestos, que así mismo darían origen a un número indefinido de composiciones, a partir de la evidencia técnica exhibida por un grupo muy pequeño de compuestos.

- La reivindicación 19 no define correctamente las características técnicas esenciales de las etapas comprendidas en el método de producción, tales como tiempo, temperatura y características de mezclado. Se sugiere definir de manera precisa las etapas del método reclamado.
- La reivindicación 20 se encuentra contenida en la reivindicación 19. Se sugiere eliminarla.
- La reivindicación 21 se encuentra contenida en la reivindicación 20. Se sugiere eliminarla.
- Las reivindicaciones 19 y 21 son repetitivas. Estas reivindicaciones reclaman un método de producción de una composición acuosa que contiene carbonato de calcio. Sin embargo, el rango reclamado en la reivindicación 21 de la sal de un catión divalente o trivalente (10-50%) se encuentra solapado con el rango reclamado en la reivindicación 19 (1-20%). Se sugiere eliminar la reivindicación 21.

Descripción (Art 28 D 486)

- La descripción hace referencia al polímero MELFLUX® o MelPers®, por ejemplo MelPers® 2450 y a los dispersantes ETHACRYL® M y MIGHTY EG®, que son marcas registradas y por tanto no definen al producto, porque su composición puede cambiar con el paso del tiempo aunque conserven el mismo nombre. Se sugiere aclarar cuáles son las características de los productos en cuestión.

Se requiere al solicitante hacer las aclaraciones y correcciones necesarias.

5. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de prioridad: marzo 23 de 2012, y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Ítem	Documento	Título	Fecha de Publicación
D1	US2004019148 (A1)	"Use of weakly anionic copolymers as dispersing and/or grinding aid agent of an aqueous suspension of mineral materials"	29/Enero/2004
D3	WO2009095697 (A1)	"IMPROVED COATED INK JET PAPER"	06/Agosto/2009

El documento D1¹ divulga el uso de un copolímero ligeramente aniónico y soluble en agua, como agente dispersante y/o un agente para ayudar a la molienda de pigmentos y/o minerales de relleno en suspensión acuosa, que dan por una parte un bajo potencial Zeta a los pigmentos y, por otro lado proporcionan una estabilización de dichas suspensiones. La invención también se refiere a dichas suspensiones acuosas de pigmentos minerales y/o rellenos y sus usos en los campos de papel, tales como la fabricación o recubrimiento de papel, y lodos de perforación utilizados para la extracción de petróleo (Resumen).

El documento D3² divulga un producto de lámina recubierto mejorado, especialmente útil en conjunción con impresoras de inyección de tinta, que comprende un sustrato que lleva un revestimiento sobre al menos una superficie, caracterizado porque el revestimiento incluye (i) un pigmento que comprende carbonato de calcio; (ii) un aglutinante para el componente (i) que comprende una proporción importante de un polímero que lleva -O-, -CO-, -OCO- y/o grupos -COO- en sus cadenas laterales; y (iii) al menos en la superficie de dicho recubrimiento, una sal soluble en agua del Grupo II, Grupo III o metales de transición (Resumen).

6. Examen de Patentabilidad (Art 14 D486)

Nivel inventivo (Art 18 D486)

La reivindicación 1 consiste en: *"Una composición acuosa que contiene carbonato de calcio, caracterizada porque comprende:..."* (Radicado N°. 14-199043-00005-0000).

Comparación de las características técnicas esenciales, con las del estado de la técnica:

Características esenciales	D1	D3
Una composición acuosa que comprende:	Una composición acuosa que comprende:	Composición que comprende
a) carbonato de calcio al menos 10 % en peso	14,3% carbonato de calcio (Pág. 26, Párr. 0716)	87,52% carbonato de calcio (Pág. 10, Tabla 4, Col. 3, Línea 5)
b) un polímero en forma de peine cargado aniónicamente	0,6 % polímero en forma de peine (Pág. 26, Párr. 0713)	No se menciona
c) opcionalmente un agente de aglutinación al menos 2.5 % en peso	42,8% agente aglutinante estireno-acrílico (Pág. 27, Párr. 0719)	Agente de aglutinación 5,71% (Pág. 10, Tabla 4, Col. 3, Línea 8)
d) una sal de un catión divalente o trivalente en una cantidad de entre 1 y 20 % en peso	No se menciona	Sulfato de manganeso 5,69% (Pág. 10, Tabla 4, Col. 3, Línea 3)

1 <http://worldwide.espacenet.com/publicationDetails/biblio?CC=US&NR=2004019148A1&KC=A1&FT=D>

2 <http://worldwide.espacenet.com/publicationDetails/biblio?CC=WO&NR=2009095697A1&KC=A1&FT=D>

El documento D1 se considera el estado de la técnica más cercano a la invención definida en la reivindicación 1 porque divulga suspensiones acuosas de pigmentos minerales y los usos de las mismas, en particular en los ámbitos de papel, como recubrimiento del papel, con la obtención, en particular, de propiedades iguales o mejores para la hoja, en particular de opacidad, brillo o capacidad de impresión (Pág. 1, Párr. 0004).

Adicionalmente, el documento D1 enseña una suspensión acuosa donde el pigmento se selecciona entre carbonato de calcio natural, tal como calcita, creta o mármol, carbonato de calcio sintético, también denominado carbonato de calcio precipitado, entre otros (Rev. 12). También, que el 73% de las partículas tienen un diámetro inferior a 1 micrómetro (Pág. 6, Párr. 0119)

Así mismo, D1 muestra que la composición además contiene 1 g de amonio 28% (Pág. 27, Párr. 0723) y 3 g de NOPCO™ NDW (Pág. 27, Párr. 0724). Por otra parte, enseña que la concentración de materia seca es del 61% (Pág. 6, Párr. 0119).

La diferencia entre la invención, definida en la reivindicación 1 y la composición divulgada en D1 consiste en que comprende una sal de un catión divalente o trivalente en una cantidad de entre 1 y 20 % en peso.

El efecto que logra incluir la sal de un catión divalente es la mejora en propiedades de la tinta a color (composición), que impacta sobre las propiedades ópticas y mecánicas de los productos finales de impresión.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así: cómo modificar la composición conocida en D1 para obtener tintas a color con mejores propiedades ópticas para aplicaciones de impresión.

Sin embargo, la utilización de sales de cationes divalentes en composiciones que se pueden usar con buen efecto en las impresoras de inyección de tinta, ya está divulgada en el documento D3 que se refiere a una composición que incluye (i) un pigmento que comprende carbonato de calcio; (ii) un aglutinante para el componente (i) que comprende una proporción importante de un polímero que lleva -O-, -CO-, -OCO- y/o grupos -COO- en sus cadenas laterales; y (iii) al menos en la superficie de dicho recubrimiento, una sal soluble en agua del Grupo II, Grupo III o metales de transición (Pág. 2, Líneas 32-34, Pág. 3, Líneas 1-3). También enseña que el carbonato de calcio puede estar en la forma de carbonato de calcio precipitado o carbonato de calcio molido, siendo preferido este último (Pág. 3, Líneas 14-15). Además, que para un acabado de alto brillo, las partículas tienen un tamaño medio de partículas de 5 micras o menos, especialmente de 2 micrómetros o menos (Pág. 3, Líneas 19-21).

Por otra parte, D3 divulga que el aglutinante comprende acetato de polivinilo, un copolímero de acetato de vinilo, alcohol de polivinilo, carboximetil celulosa, hidroximetil celulosa, hidroxietil celulosa, alginato de sodio, y/o almidón (Rev. 8). Además, que la sal comprende una sal de calcio, magnesio, aluminio, manganeso o zinc, como cloruro de calcio, sulfato de manganeso o sulfato de magnesio (Rev. 10-11). También, que la composición contiene aglutinante, ajustador de pH, pigmento, modificador reológico, antiespumante, entre otros (Pág. 7, Tabla 1).

En consecuencia, la persona del oficio normalmente versada en la materia, incluiría las sales de cationes divalentes del documento D3 en la composición divulgada en el documento D1 para llegar así al objeto de la reivindicación 1 de la solicitud. Por lo cual se considera obvia.

Puesto que las reivindicaciones dependientes 2 – 18 no mencionan características inventivas adicionales tampoco se pueden considerar inventivas.

Las reivindicaciones 1 – 18 cumplen el requisito de novedad (Art. 16), pero no cumplen

con el requisito de nivel inventivo (Art. 18).

La reivindicación 19 consiste en: *“Un método de producción de una composición acuosa que contiene carbonato de calcio, de conformidad con cualquiera de las reivindicaciones 1 a 18, caracterizado porque comprende las etapas de:...”* (Radicado N°. 14-199043-00005-0000).

Comparación de las características técnicas esenciales, con las del estado de la técnica:

Características esenciales	D1	D3
Un método de producción de una composición acuosa de las reivindicaciones 1 a 18, comprende las etapas de:	Método de obtención de la composición	Método de obtención de la composición
a) proveer agua	62,7 g de agua (Pág. 26, Párr. 0712)	Agua (Pág. 10, Línea 5)
b) proveer un material que contiene carbonato de calcio.	150 g carbonato de calcio (Pág. 26, Párr. 0716)	Setacarb 80 (Pág. 10, Tabla 4, Fila 5)
c) proveer al menos un polímero en forma de peine cargado aniónicamente	653 g polímero en forma de peine (Pág. 26, Párr. 0713)	No se menciona
d) opcionalmente proveer al menos un agente de aglutinación en una cantidad de al menos 2.5 % en peso	450 g (42,8%) aglutinante de estireno-acrílico (Pág. 27, Párr. 0719)	alcohol de polivinilo (Pág. 10, Tabla 4, Fila 4)
e) proveer al menos una sal de un catión divalente o trivalente, en una cantidad de entre 1 y 20 % en peso	No se menciona	Sulfato de manganeso 5,69% (Pág. 10, Tabla 4, Fila 3)
f) poner en contacto el material etapa b) con el agua de la etapa que contiene carbonato de calcio de la a)	Agitar durante 20 min agua, carbonato de calcio y el polímero en forma de peine (Pág. 27, Párr. 0718)	No se menciona
g) poner en contacto el material que contiene carbonato de calcio de la etapa b) con al menos un polímero en forma de peine cargado aniónicamente de la etapa c) antes y/o durante y/o después de la etapa f)		No se menciona
h) opcionalmente poner en contacto el material que contiene carbonato de calcio de la etapa b) con al menos un agente de aglutinación de la etapa d) antes y/o durante y/o después de la etapa f) y/o antes y/o durante y/o después de la etapa g)	Posteriormente, adicionar a la mezcla anterior el agente de aglutinación (Pág. 27, Párr. 0718-0719)	Setacarb 80 se adiciona al alcohol polivinílico (Pág. 10, Línea 9)
i) poner en contacto el material que contiene carbonato de calcio de la etapa b) con al menos una sal del catión divalente o trivalente de la etapa e) antes o después de la etapa g)	No se menciona	Adicionar la solución de sulfato de manganeso al alcohol polivinílico (Pág. 10, Líneas 6-7)

El documento D1 se considera el estado de la técnica más cercano a la invención definida en la reivindicación 19 porque divulga un procedimiento para la preparación de una suspensión de carbonato de calcio, utilizada como pigmento para papel (Pág. 1, Párr 0004, Pág. Pág 6, Párr 0118).

Adicionalmente, enseña que el contenido sólido del pigmento de recubrimiento es de aproximadamente 65% (Pág. 28, Párr. 0757).

Es importante destacar que los literales a) a e) de la reivindicación 19, no corresponden a características técnicas esenciales de un método de producción de una composición acuosa, ya que únicamente se enlistan los reactivos que se emplean en las etapas f) a i). Sin embargo, se encuentran presentes en la tabla comparativa para poder realizar el análisis de una forma más clara, debido a la forma en la que se encuentran descritas las etapas f) a i).

La diferencia entre la invención, definida en la reivindicación 19 y el procedimiento divulgado en D1 consiste en poner en contacto las mezclas con una sal del catión divalente o trivalente.

El efecto que logra incluir esta etapa no puede ser evidenciado porque no existe información en la descripción que lo permita.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así: cómo modificar el procedimiento conocido en D1 para conseguir un procedimiento alternativo para producir una composición acuosa de carbonato de calcio.

Sin embargo, adicionar sulfato de manganeso a composiciones de pigmentos acuosas de carbonato de calcio, ya está divulgado en el documento D3 que se refiere a un procedimiento para preparar una composición para recubrir una hoja de papel (Pág. 7, Líneas 14-15).

Adicionalmente, el documento D3 muestra que la sal de sulfato de magnesio se puede encontrar en una concentración de 12,22% en peso (Pág. 8, Tabla 2, Col. 3, Línea 3, característica mencionada en la reivindicación 15 de la presente solicitud).

En consecuencia, la persona del oficio normalmente versada en la materia, incluiría la adición de sulfato de manganeso del documento D3 en el procedimiento divulgado en el documento D1 para llegar así al objeto de la reivindicación 19 de la solicitud. Por lo cual se considera obvia.

Puesto que las reivindicaciones dependientes 20 – 25 no mencionan características inventivas adicionales tampoco se pueden considerar inventivas.

Las reivindicaciones 1 – 25 cumplen el requisito de novedad (Art. 16), pero no cumplen con el requisito de nivel inventivo (Art. 18).

7. Conclusión

Los requisitos de Patentabilidad de la presente solicitud están afectados así:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US2004019148 (A1)	1 a 25	Nivel Inventivo
D3	WO2009095697 (A1)	1 a 25	Nivel inventivo

8. Respuesta a los argumentos de la solicitante

Argumentos con respecto al capítulo reivindicatorio

1. El solicitante argumenta que “...*el capítulo reivindicatorio es claro y se encuentra debidamente soportado ya que una persona normalmente versada en la materia identificaría lo que comprende un «material que contiene carbonato de calcio», un «polímero en forma de peine cargado aniónicamente», un «agente de aglutinación» y una «sal de un catión divalente o trivalente», teniendo en cuenta que esos componentes se encuentran definidos tanto en la descripción como en el capítulo reivindicatorio de la presente solicitud...*”.

Se aclara que el capítulo reivindicatorio es claro, ya que la persona normalmente versada en la materia conoce términos como “*agente de aglutinación*” o “*sal de un catión divalente o trivalente*”. Sin embargo, no es conciso, ya que los términos mencionados anteriormente encierran una gran cantidad de componentes que no son una razonable generalización del tipo de compuestos que han sido ensayados.

Si bien estos términos son definidos en reivindicaciones dependientes, se sugiere definirlos adecuadamente en la reivindicación independiente, para poder comparar adecuadamente la invención con el estado de la técnica.

2. El solicitante afirma que *“Adicionalmente, me permito hacer énfasis en que es la carga específica y no la estructura química la que determina sin un polímero en forma de peine es adecuado o no para la presente invención, por lo que la incorporación de fórmulas químicas específicas en la reivindicación 1 constituiría una limitación injustificada...”*.

Se aclara que si bien el polímero en forma de peine interactúa con las partículas de carbonato de calcio mediante interacciones electrostáticas, gracias a que el polímero presenta una carga negativa y el carbonato de calcio posee carga positiva, la carga negativa que posee el polímero se obtiene como resultado de su estructura química, por lo que es necesario definir el polímero en forma de peine mediante una fórmula química.

3. El solicitante sostiene que *“...me permito indicar que la viscosidad corresponde a una característica funcional usual para caracterizar una composición acuosa, y no a un resultado a alcanzar, permitiendo así una mejor diferenciación de la composición reclamada de lo divulgado en el estado del arte”*.

Se aclara que la viscosidad es una propiedad física de la composición, que es dependiente de la estructura molecular, composición, temperatura y presión³. De esta forma, el valor de un parámetro, como la viscosidad, no define correctamente a la composición que se encuentra siendo reclamada, la cual debe ser definida por el nombre o fórmula química de cada uno de sus componentes y la proporción en la que se encuentran cada uno de ellos.

Argumentos con respecto al estudio de nivel inventivo

1. El solicitante reitera que *“...la característica distintiva (presencia de una sal de cationes divalentes o trivalentes) tiene un efecto técnico que es claramente ejemplificado en la descripción de la presente solicitud... Por lo tanto, el problema técnico objetivo subyacente en la presente invención en vista del documento D1 como el estado del arte más cercano no es obtener una composición acuosa que contenga carbonato de calcio alternativa como asegura el Señor Examinador sino proveer una composición acuosa que contiene carbonato de calcio que permite una capacidad de impresión mejorada para tintas a color”*.

Se aclara que el solicitante tiene razón, en la descripción de la presente solicitud (Radicado N° 14-199043-00000-0000, Pág. 62, Párr. 1), se muestra el efecto que presenta la sal de cationes divalentes o trivalentes sobre los pigmentos, por lo que el problema técnico no es encontrar una composición de pigmentos alternativa. Debido a esto, se realizó un nuevo examen de patentabilidad, teniendo en cuenta el efecto de la sal de cationes divalentes o trivalentes sobre la composición.

3 http://link.springer.com/chapter/10.1007/978-94-009-2163-4_1 Introduction to Rheology, en Melt Rheology And Its Role In Plastics Processing. Dealy, J.M. et al. Van Nostrand Reinhold. 1990. Pág. 3, Párr. 1.

Argumentos con respecto a D2

1. El solicitante sostiene “...el documento D2 se refiere a un proceso específico de molienda en seco y no a la capacidad de impresión para tintas a color. Por tanto, es altamente cuestionable que la persona normalmente en la materia consultaría el documento D2 para resolver el problema técnico objetivo subyacente en la reivindicación 1 en vista del documento D1”.

Se aclara que el solicitante tiene razón, el documento D2 se refiere a un proceso de molienda en seco. Por esta razón se realizó un nuevo examen de patentabilidad, empleando el documento D3, como estado de la técnica pertinente para compararlo con los pigmentos que comprenden carbonato de calcio y sus métodos de preparación, ahora reivindicados.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Si como respuesta a este requerimiento el solicitante llegara a modificar: i) el capítulo reivindicatorio, ii) la descripción de la invención a proteger, iii) o presente un nuevo capítulo reivindicatorio, y desee que se realice un nuevo examen de patentabilidad a esta modificación, no deberá pagar la tasa de modificación voluntaria pero sí la correspondiente a la tasa de examen de patentabilidad. En todo caso, el número de requerimientos por no patentabilidad estará supeditado a que el término del estudio de patentabilidad no sea superior a 18 meses, contados desde la publicación de la solicitud de patente de invención. Adicionalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones deberá pagar la tasa por reivindicación adicional.

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



JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (c)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2016-06-21

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(19) **United States**(12) **Patent Application Publication**
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(43) **Pub. Date: Jan. 29, 2004**(54) **USE OF WEAKLY ANIONIC COPOLYMERS
AS DISPERSING AND/OR GRINDING AID
AGENT OF AN AQUEOUS SUSPENSION OF
MINERAL MATERIALS****Publication Classification**(51) **Int. Cl.⁷ C08L 31/00**
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ALEXANDRIA, VA 22314 (US)**(21) **Appl. No.: 10/311,219**(22) **PCT Filed: Jun. 12, 2001**(86) **PCT No.: PCT/FR01/01804**(30) **Foreign Application Priority Data**

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(57) **ABSTRACT**

The invention relates to the use of a slightly anionic and water-soluble copolymer, as a dispersing agent and/or an agent for assisting the grinding of pigments and/or mineral fillers in aqueous suspension giving on the one hand a low Zeta potential to the aqueous suspensions of the said fillers and/or pigments and on the other hand affording an electro-steric stabilisation of the said suspensions.

The invention also relates to the said aqueous suspensions of mineral pigments and/or fillers and their uses in the fields of paper, such as the manufacture or coating of paper, and drilling muds used for petroleum prospecting or extraction.

The invention also relates to the use of the said dispersing agents and/or agent for assisting the grinding in the field of paints and plastic materials such as thermoplastic or thermosetting resins.

**USE OF WEAKLY ANIONIC COPOLYMERS AS
DISPERSING AND/OR GRINDING AID AGENT OF
AN AQUEOUS SUSPENSION OF MINERAL
MATERIALS**

[0001] The present invention relates to the technical sector of mineral fillers, notably for papermaking applications, and their appropriate processing in order to improve either the method of manufacturing the paper sheet, or its properties.

[0002] The invention firstly relates to the use of a slightly anionic and water-soluble copolymer as a dispersing agent and/or an aid to the grinding of mineral pigments and/or fillers in aqueous suspension giving on the one hand a low Zeta potential to the aqueous suspensions of the said fillers and/or pigments and on the other hand affording electro-steric stabilisation of the said suspensions.

[0003] The invention also relates to the said slightly anionic water-soluble agent, dispersing agent and/or aid to the grinding of mineral pigments and/or fillers in aqueous suspension giving on the one hand a low Zeta potential to the aqueous suspensions of the said fillers and/or pigments and on the other hand affording electro-steric stabilisation of the said suspensions.

[0004] The invention also relates to the said aqueous suspensions of mineral pigments and/or fillers and the uses thereof notably in the fields of paper, such as amongst other things the manufacture or coating of the paper, with the obtaining in particular of equal or better properties for the sheet, and notably opacity, gloss or printability, or notably in the field of drilling muds used in prospecting for oil or in oil extraction. The invention also concerns the use of the said slightly anionic water-soluble dispersing agent and/or aid to the grinding in the fields of paints or plastic materials such as thermoplastic or thermosetting resins. Then, the invention relates to the manufactured papers and/or coated papers with the use of the said aqueous suspensions of mineral pigments and/or fillers as well as relates to the drilling muds containing the said aqueous suspensions of mineral pigments and/or fillers.

[0005] This is because, in the manufacture of paper, it is becoming more and more usual to replace some of the cellulose fibres, which are expensive, with mineral fillers and/or pigments, which are less expensive, in order to reduce the cost of the paper whilst improving, for example, its opacity, its whiteness or its properties of printability.

[0006] The mineral fillers and/or pigments such as, for example, natural or synthetic calcium carbonate, dolomites, magnesium hydroxide, kaolin, talc, gypsum, titanium oxide or aluminium hydroxide are normally incorporated in the sheet of paper during its formation on the wire.

[0007] This is achieved by incorporating the mineral filler and/or pigment, either in powder form or in aqueous suspension, in the papermaking pulp in such a way that the pulp is drained onto the wire and the particles of mineral fillers and/or pigments in suspension are retained in the fibrous sheet obtained. Since this retention is not complete, this leads the papermaker to use chemical additives and the manufacturers of fillers to use surface treatment agents for these mineral materials.

[0008] Likewise, when the sheet of paper is treated by coating, the papermaker uses, in his formulation, mineral materials generally put in suspension, either by the papermaker himself or by the manufacturer, using anionic additives such as for example polyacrylates or polyphosphates or others or using cationic additives such as for example cationised polyacrylates or polymethacrylates such as quaternary dimethylaminoethyl methacrylates or melamine-formaldehyde resins, epichlorhydrine resins, dicyandiamide resins or others.

[0009] Thus the skilled man in the art knows agents assisting grinding or water-soluble dispersing agents (FR 2 488 814, FR 2 603 042, EP 0 100 947, EP 0 100 948, EP 0 129 329, EP 0 542 643, EP 0 542 644) consisting of polymers and/or copolymers of the anionic type for producing aqueous suspensions of mineral pigments and/or fillers. However, these have the drawback of requiring the addition of cationic compounds during the process of manufacturing the sheet of paper when they are used in these sheet manufacturing operations, and result in coated papers with an opacity which does not meet the opacity required by the final use when they are used in paper coating operations.

[0010] Moreover, the skilled man in the art knows agents for assisting grinding or water-soluble dispersing agents (ED 0 281 134, EP 0 307 795) consisting of polymers and/or copolymers of the cationic type for producing aqueous suspensions of mineral pigments and/or fillers which present the major risk of incompatibility with any anionic medium present in the papermaking formulations, which may go as far as the caking of the medium, thus blocking production entirely.

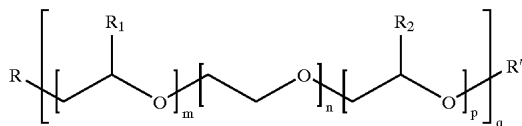
[0011] Another solution is known to the skilled man in the art for arriving at aqueous suspensions of mineral pigments and/or fillers which are stable over time and have a high concentration of dry matter at the same time as a fine particle size.

[0012] This solution (WO 91/09067) consists in using amphoteric water-soluble copolymers as a weakly anionic water-soluble dispersing agent and/or aid to the grinding of pigments and/or mineral fillers. However, such copolymers have the drawback of being sensitive to the pH and ionic strength of the medium and also being easily hydrolysable.

[0013] Thus the skilled man in the art is confronted with the problem of obtaining aqueous suspensions of mineral fillers and/or pigments which are refined, stable over time, with a moderate to high concentration of mineral material, which do not present any risk of incompatibility in papermaking formulations, only slightly sensitive to the pH and ionic strength of the media used in papermaking formulations and to the problem of obtaining suspensions making it possible to arrive at sheet properties meeting the criteria of the final user, a problem which none of the solutions available to him completely resolve.

[0014] Bearing in mind the aforementioned drawbacks concerning anionic or cationic aqueous suspensions or aqueous suspensions obtained by means of amphoteric agents,

the Applicant unexpectedly found that the presence in the copolymer of at least one monomer of formula (I)



[0015] in which

[0016] m and p represent a number of alkylene oxide units less than or equal to 150,

[0017] n represents a number of ethylene oxide units less than or equal to 150,

[0018] q represents a number at least equal to 1 and such that

$$5 \leq (m+n+p)q \leq 150$$

[0019] R₁ is hydrogen or the methyl or ethyl radical

[0020] R₂ is hydrogen or the methyl or ethyl radical

[0021] R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as for example acrylurethane, methacrylurethane, α-α' dimethylisopropenyl benzylurethane or allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

[0022] R' represents a hydrocarbon radical having 1 to 5 carbon atoms

[0023] made possible the development of weakly anionic water-soluble copolymers allowing electro-steric stabilisation thus resulting in the obtaining of aqueous suspensions of mineral pigments and/or fillers resolving the problems set out above, that is to say resulting, notably, in the obtaining of aqueous suspensions of mineral pigments and/or fillers with a moderate to high mineral matter content, stable over time, without sedimentation, only slightly sensitive to the pH and ionic strength of the media used in the papermaking or petroleum formulations, and having a low Zeta potential.

[0024] Thus the prior art essentially describes dispersing agents and/or grinding aid agents which are anionic, cationic or amphoteric or weakly anionic and water-soluble.

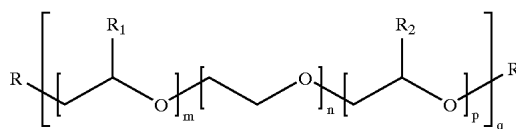
[0025] In fact European patent application EP 0 870 784 describes slightly anionic agents, but these agents give aqueous suspensions with a high Zeta potential and do not resolve the problem posed for the final user.

[0026] Thus, according to the invention, the dispersing agent and/or grinding aid agent is distinguished from the prior art in that it is composed of

[0027] a) at least one anionic monomer with a monocarboxylic function

[0028] b) possibly at least one anionic monomer with a dicarboxylic function or with a sulphonic or phosphoric or phosphonic function or a mixture thereof

[0029] c) at least one non-ionic monomer, the non-ionic monomer consisting of at least one monomer of formula (I):



[0030] in which

[0031] m and p represent a number of alkylene oxide units less than or equal to 150,

[0032] n represents a number of ethylene oxide units less than or equal to 150,

[0033] q represents a number at least equal to 1 and such that

$$5 \leq (m+n+p)q \leq 150$$

[0034] R₁ is hydrogen or the methyl or ethyl radical

[0035] R₂ is hydrogen or the methyl or ethyl radical

[0036] R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as for example acrylurethane, methacrylurethane, α-α' dimethylisopropenyl benzylurethane or allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

[0037] R' represents a hydrocarbon radical having 1 to 5 carbon atoms

[0038] d) possibly a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, alphamethylstyrene and derivatives thereof, and

[0039] e) possibly at least one monomer having at least two unsaturated ethylenic chains referred to in the remainder of the application as across-linking monomer

[0040] giving the properties of low Zeta potential and electro-steric stability to the suspensions.

[0041] These aims are achieved by means of the use, as a dispersing agent and/or a grinding aid agent, of a copolymer consisting of:

[0042] a) at least one anionic monomer with an unsaturated ethylenic chain and with a monocarboxylic function

[0043] b) possibly at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof

[0044] c) at least one non-ionic monomer of formula (I) and

[0045] d) possibly a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers with unsaturated ethylenic chains such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, aliphatic styrene and derivatives thereof,

[0046] e) possibly at least one cross-linking monomer

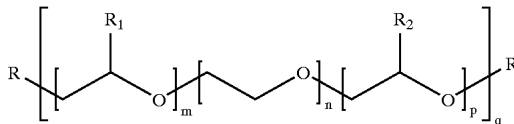
[0047] the total of constituents a), b), c), d) and e) being equal to 100%, with moreover the obligatory presence of a monomer of type a) in order to be able to ensure the dispersion of the mineral materials with a high and medium concentration of dry matter and the obligatory presence of a monomer of type c) in combination with the monomer of type a) in order to ensure the electro-steric stabilisation of the aqueous suspensions of mineral materials with a high and medium concentration of dry matter.

[0048] The use according to the invention of a weakly anionic and water-soluble copolymer as a dispersing agent and/or a grinding aid agent for mineral pigments and/or fillers in aqueous suspension is characterised in that the said copolymer consists of:

[0049] a) at least one anionic monomer with an unsaturated ethylenic chain and a monocarboxylic function chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid or diacid hemiesters such as the C₁ to C₄ monoesters of maleic or itaconic acids, or mixtures thereof,

[0050] b) possibly at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof chosen from amongst monomers with an unsaturated ethylenic chain and a dicarboxylic function such as crotonic, isocrotonic, cinnamic, itaconic, maleic or citraconic acid or carboxylic acid anhydrides, such as maleic anhydride, or chosen from amongst monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methylpropane sulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as vinyl phosphoric acid, ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphonic function such as phosphonic vinyl acid, or mixtures thereof

[0051] c) at least one non-ionic monomer with an



[0052] unsaturated ethylenic chain of formula (I):

[0053] in which

[0054] m and p represent a number of alkylene oxide units less than or equal to 150,

[0055] n represents a number of ethylene oxide units less than or equal to 150,

[0056] q represents a number at least equal to 1 and such that

$$5 \leq (m+n+p)q \leq 150$$

[0057] R₁ is hydrogen or the methyl or ethyl radical

[0058] R₂ is hydrogen or the methyl or ethyl radical

[0059] R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as for example acrylurethane, methacrylurethane, α-α' dimethylisopropenyl benzylurethane or allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

[0060] R' represents a hydrocarbon radical having 1 to 5 carbon atoms

[0061] d) possibly a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, aliphatic styrene and derivatives thereof, and

[0062] e) possibly at least one cross-linking monomer chosen non-limitatively from the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, allyl maleates, methylenebisacrylamide, methylenebismethacrylamide, tetrallyloxyethane, the triallylcyanurates, and the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose and others,

[0063] the total of constituents a), b), c), d) and e) being equal to 100%

[0064] and in that the said copolymer has a specific viscosity of no more than 10, preferably no more than 5 and highly preferentially no more than 2.

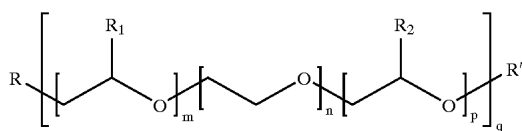
[0065] More particularly the use of the aforementioned copolymer is characterised in that the said copolymer consists, expressed by weight, of:

[0066] a) 2% to 85% and even more particularly 2% to 80% of at least one anionic monomer with an

unsaturated ethylenic chain and a monocarboxylic function chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid or the hemiesters of diacids such as the C₁ to C₄ monoesters of maleic or itaconic acids, or mixtures thereof,

[0067] b) from 0% to 80% and even more particularly from 0% to 50% and very particularly from 0% to 20% of at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof chosen from amongst monomers with an unsaturated ethylenic chain and a dicarboxylic function such as crotonic, isocrotonic, cinnamic, itaconic, maleic or citraconic acid or carboxylic acid anhydrides, such as maleic anhydride, or chosen from amongst monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methyl-propane sulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as vinyl phosphoric acid, ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphonic function such as phosphonic vinyl acid, or mixtures thereof

[0068] c) from 20% to 95% of at least one monomer with an unsaturated ethylenic chain of formula (I):



[0069] in which

[0070] m and p represent a number of alkylene oxide units less than or equal to 150,

[0071] n represents a number of ethylene oxide units less than or equal to 150,

[0072] q represents a number at least equal to 1 and such that

$$5 \leq (m+n+p)q \leq 150$$

[0073] R₁ is hydrogen or the methyl or ethyl radical

[0074] R₂ is hydrogen or the methyl or ethyl radical

[0075] R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as for example acrylurethane, methacrylurethane, α-α' dimethylisopropenyl benzylurethane or allylurethane, and to the

group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

[0076] R' represents a hydrocarbon radical having 1 to 5 carbon atoms

[0077] d) from 0% to 50% of a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, aliphatic styrene and derivatives thereof, and

[0078] e) from 0% to 3% of at least one cross-linking monomer chosen non-limitatively from the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, allyl maleates, methylenebisacrylamide, methylenebis-methacrylamide, tetraallyloxyethane, the triallylcyanurates, or the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose or others,

[0079] the total of constituents a), b), c), d) and e) being equal to 100%

[0080] and in that the said copolymer has a specific viscosity of no more than 10, preferably no more than 5 and highly preferentially no more than 2.

[0081] Even more preferentially, the use of the copolymer is characterised in that

[0082] a) the anionic monomer with unsaturated ethylenic chains and monocarboxylic function is preferably chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid,

[0083] b) the anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof is preferably chosen from amongst the monomers with an unsaturated ethylenic chain and a dicarboxylic function such as diacids including itaconic or maleic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methyl-propanesulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or mixtures thereof

[0084] c) the non-ionic monomer with an unsaturated ethylenic chain of formula (I) is such that

[0085] R₁ represents hydrogen or the methyl or ethyl radical

[0086] R₂ represents hydrogen or the methyl or ethyl radical

[0087] R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic

esters as well as unsaturated urethanes such as for example acrylurethane, methacrylurethane, α - α' dimethylisopropenyl benzylurethane, allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

[0088] R' represents a hydrocarbon radical having 1 to 5 carbon atoms

[0089] d) the monomer of the acrylamide or methacrylamide type or derivatives thereof is chosen from amongst acrylamide or methacrylamide, and the non water-soluble monomer is chosen from amongst ethyl acrylate or styrene

[0090] e) the cross-linking agent is chosen from amongst the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, the allyl maleates, methylenebisacrylamide, methylenebismethacrylamide, tetraallyloxyethane, the triallylcyanurates, the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose or others.

[0091] The copolymer used according to the invention is obtained by known methods of radical copolymerisation in solution, in direct or reverse emulsion, in suspension or precipitation in suitable solvents, in the presence of catalytic systems and known transfer agents.

[0092] This copolymer obtained in acid form and possibly distilled can also be partially or completely neutralised by one or more neutralisation agents having a monovalent neutralising function or a polyvalent neutralising function such as for example, for the monovalent function, those chosen from the group consisting of alkali cations, in particular sodium, potassium, lithium, ammonium or the aliphatic and/or cyclic primary, secondary or tertiary amines such as for example stearylamine, the ethanolamines (mono-, di, triethanolamine), mono and diethylamine, cyclohexylamine, methylcyclohexylamine or, for the polyvalent function, those chosen from the group consisting of alkaline-earth divalent cations, in particular magnesium and calcium, or zinc, also consisting of trivalent cations, in particular aluminium, or certain cations with a higher valency.

[0093] Each neutralisation agent then acts according to the degrees of neutralisation peculiar to each valency function.

[0094] According to another variant, the copolymer resulting from the copolymerisation reaction can, possibly before or after the complete or partial neutralisation reaction, be treated and separated into several phases, according to static or dynamic methods known to experts, by means of one or more polar solvents belonging notably to the group consisting of water, methanol, ethanol, propanol, isopropanol, the butanols, acetone, tetrahydrofuran or mixtures thereof.

[0095] One of the phases then corresponds to the copolymer used according to the invention as a dispersing agent and/or a grinding aid agent for mineral materials in aqueous suspension.

[0096] The specific viscosity of the copolymer is symbolised by the letter η and is determined as follows:

[0097] A solution of polymerisate is taken so as to obtain a solution corresponding to 2.5 g of dry polymer neutralised with soda and to 50 ml of a solution of bipermuted water.

Then, with a capillary viscometer with a Baume constant of 0.000105 placed in a bath thermostatically controlled at 25° C., a measurement is made of the run-out time for a given volume of the aforementioned solution containing the copolymer, and the run-out time for the same volume of the solution of bipermuted water without the said copolymer. It is then possible to define the specific viscosity η by means of the following equation:

$$\eta = \frac{\text{(run-out time of the polymer solution)} - \text{(run-out time of the permuted water solution)}}{\text{(run-out time of the permuted water solution)}}$$

[0098] The capillary tube is generally chosen so that the run-out time of the permuted water solution with no copolymer is approximately 60 to 100 seconds, thus giving specific viscosity measurements with very good precision.

[0099] The invention also relates to the said water-soluble, weakly anionic agent, dispersing agent and/or grinding aid agent for pigments and/or mineral fillers in aqueous suspension giving on the one hand a low Zeta potential to the aqueous suspensions of the said fillers and/or pigments and on the other hand affording an electro-steric stabilisation of the said suspensions. This agent is characterised in that it is the previously described copolymer.

[0100] The aqueous suspensions of fillers and/or pigments according to the invention are characterised in that they contain the said agent and more particularly in that they contain from 0.05% to 5% by dry weight of the said agent with respect to the total dry weight of the fillers and/or pigments, and even more particularly 0.3% to 1.0% by dry weight of the said agent with respect to the total dry weight of the fillers and/or pigments.

[0101] They are also characterised in that the filler and/or pigment is chosen from amongst natural calcium carbonate such as notably calcite, chalk or marble, synthetic calcium carbonate named precipitated calcium carbonate, dolomites, magnesium hydroxide, kaolin, talc, gypsum, titanium oxide, or aluminium hydroxide or any other filler and/or pigment normally used in the papermaking or petroleum field.

[0102] Finally, they are characterised in that they are only slightly sensitive to the pH and ionic strength of the media and in that they have a low Zeta potential, that is to say a Zeta potential of between 0 and -30 mV and preferentially between 0 and -20 mV.

[0103] The papers manufactured and/or coated according to the invention are characterised in that they contain the said aqueous suspensions of fillers and/or pigments according to the invention.

[0104] The drilling muds according to the invention are characterised in that they contain the said aqueous suspensions of fillers and/or pigments according to the invention.

[0105] In practice, the dispersing operation, also referred to as the operation of dispersing the mineral filler to be dispersed, can be effected in two different ways.

[0106] One of the ways consists in effecting, under agitation, the preparation of a suspension of mineral filler and/or pigment by introducing all or part of the dispersing agent

according to the invention into the aqueous phase, and then the mineral material, so as to obtain an aqueous suspension with a moderate to high mineral material content, stable over time, without sedimentation, only slightly sensitive to the pH and ionic strength of the media used in the papermaking formulations, and having a low Zeta potential, that is to say a Zeta potential of between 0 and -30 mV and preferentially between 0 and -20 mV.

[0107] Another way consists in preparing the suspension of mineral filler and/or pigment by introducing into the mineral filler and/or pigment cake all the quantity of dispersing agent to be tested so as to obtain an aqueous suspension with a moderate to high mineral material content, stable over time, without sedimentation, only slightly sensitive to the pH and ionic strength of the media used in the papermaking formulations, and having a low Zeta potential, that is to say a Zeta potential of between 0 and -30 mV and preferentially between 0 and -20 mV.

[0108] This dispersing operation can follow on from the grinding operation described below or can be implemented completely independently.

[0109] Thus, in practice, the operation of grinding the mineral material to be refined consists in grinding the mineral substance with a grinding substance of very fine particles in an aqueous medium containing the grinding aid agent.

[0110] To the aqueous suspension of the mineral substance to be ground, the grinding substance with a particle size advantageously between 0.20 and 4 millimetres is added. The grinding substance is generally in the form of particles of materials which are as diverse as silicon oxide, aluminium oxide, zirconium oxide or mixtures thereof, and synthetic resins with high hardness, steels, or others. An example of the composition of such grinding substances is given by the patent FR 2 303 681, which describes the grinding element formed by 30% to 70% by weight zirconium oxide, 0.1% to 5% aluminium oxide and 5% to 20% silicon oxide.

[0111] The grinding substance is preferably added to the suspension in a quantity such that the ratio by weight between this grinding material and the mineral substance to be ground is at least 2/1, this ratio preferably being between the limits 3/1 and 5/1.

[0112] The mixture of the suspension and grinding substance is then subjected to the mechanical action of stirring, such as the one which occurs in a conventional grinder with microelements.

[0113] The time required for achieving the required fineness of the mineral substance after grinding varies according to the nature and quantity of the mineral substances to be ground, and according to the stirring mode used and the temperature of the medium during the grinding operation.

[0114] The aqueous suspensions thus obtained can be used in the field of paper in mass filling or in coating with a low Zeta potential.

[0115] During the manufacture of the sheet of paper, that is to say during their use as a mass filler, these suspensions can be used with the coating broke.

[0116] They can also be used in the field of drilling muds such as for example soft bentonitic muds, saturated salt muds and sea-water muds.

[0117] The scope and interest of the invention will be perceived more clearly by means of the following examples, which are not limitative.

EXAMPLE 1

[0118] This example relates to the preparation of a calcium carbonate suspension by simple dispersion and the revealing of the properties afforded by the presence of at least one monomer of formula (I) in the non-ionic monomer.

[0119] To this end, for each of the following tests, carried out using a marble filtration cake in which 73% of the particles have a diameter less than 1 micrometre determined by measurement using the Sedigraph™ 5100 from Micromeritics, the aqueous suspension of marble is prepared by the introduction, into the cake, of the necessary quantity by dry weight of dispersion agent to be tested with respect to the dry weight of the said cake to be put in suspension in order to obtain an aqueous suspension of calcium carbonate with a dry matter concentration of 61%.

[0120] After 20 minutes stirring, a sample of the suspension of calcium carbonate obtained is recovered in a flask and the Brookfield™ viscosity is measured by means of a Brookfield™ type RVT viscometer, at a temperature of 25° C. and a speed of rotation of 10 and 100 revolutions per minute with the appropriate spindle.

[0121] After a time of 8 days in the flask, the Brookfield™ viscosity of the suspension is measured by introducing, into the unstirred flask, the appropriate spindle of the Brookfield™ type RVT viscometer, at a temperature of 25° C. and a speed of rotation of 10 revolutions and 100 revolutions per minute (BS viscosity Brookfield™ viscosity before stirring).

[0122] The same Brookfield™ viscosity measurements are also made once the flask has been stirred and constitute the results of Brookfield™ viscosity after stirring (AS viscosity).

[0123] For measuring the Zeta potential, a sample of the suspension of calcium carbonate obtained is also recovered, after the 20 minutes of stirring, and a few drops of this is dispersed in a sufficient quantity of serum obtained by mechanical filtration of the said suspension in order to obtain a colloidal suspension which is scarcely cloudy.

[0124] This suspension is introduced into the measuring cell of the Zetamaster S Zetameter from Malvern, which directly displays the value of the Zeta potential in mV.

[0125] These different measurements were carried out for the following tests.

[0126] Test N° 1:

[0127] This test, illustrating the prior art, used 0.7% by dry weight of a sodium polyacrylate with a specific viscosity of 4.80.

[0128] Test N° 2:

[0129] This test, illustrating the prior art, used 0.7% by dry weight of an acrylic acid-maleic anhydride copolymer completely neutralised with soda and with a specific viscosity of 1.38.

[0130] Test N° 3:

[0131] This test, illustrating a field outside the invention, used 0.7% by dry weight of a homopolymer, with a specific viscosity of 0.91 and whose single monomer is a monomer of formula (I) in which:

[0132] R_1 represents hydrogen

[0133] R_2 represents hydrogen

[0134] R represents the methacrylate group

[0135] R' represents the methyl radical

[0136] with $(m+n+p)q=45$.

[0137] Test N° 4:

[0138] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.28 and consisting of:

[0139] a) 8.0% by weight acrylic acid as an anionic monomer with a monocarboxylic function

[0140] b) 5.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0141] c) 82.0% by weight of a monomer of formula (I) in which:

[0142] R_1 represents hydrogen

[0143] R_2 represents hydrogen

[0144] R represents the methacrylurethane group

[0145] R' represents the methyl radical

[0146] d) 4.5% by weight ethyl acrylate

[0147] with $(m+n+p)q=113$.

[0148] Test N° 5:

[0149] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.78 and consisting of:

[0150] a) 8.0% by weight acrylic acid as an anionic monomer with a monocarboxylic function

[0151] b) 5.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0152] c) 75.0% by weight of a monomer of formula (I) in which

[0153] R_1 represents hydrogen

[0154] R_2 represents hydrogen

[0155] R represents the methacrylurethane group

[0156] R' represents the methyl radical

[0157] d) 11.5% by weight ethyl acrylate

[0158] with $(m+n+p)q=40$.

[0159] Test N° 6:

[0160] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.51 and consisting of:

[0161] a) 8.0% by weight acrylic acid as an anionic monomer with a monocarboxylic function

[0162] b) 5.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0163] c) 71.0% by weight of a monomer of formula (I) in which

[0164] R_1 represents hydrogen

[0165] R_2 represents hydrogen

[0166] R represents the methacrylurethane group

[0167] R' represents the methyl radical

[0168] d) 15.5% by weight ethyl acrylate

[0169] with $(m+n+p)q=25$.

[0170] Test N° 7:

[0171] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.51 and consisting of:

[0172] a) 8.0% by weight acrylic acid as an anionic monomer with a monocarboxylic function

[0173] b) 5.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0174] c) 67.0% by weight of a monomer of formula (I) in which

[0175] R_1 represents hydrogen

[0176] R_2 represents hydrogen

[0177] R represents the methacrylurethane group

[0178] R' represents the methyl radical

[0179] d) 19.5% by weight ethyl acrylate

[0180] with $(m+n+p)q=17$.

[0181] Test N° 8:

[0182] This test, illustrating the invention, used 0.6% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.56 and consisting of:

[0183] a) 2.0% by weight methacrylic acid as an anionic monomer with a monocarboxylic function

[0184] b) 13.0% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0185] c) 85.0% by weight of a monomer of formula (I) in which

[0186] R_1 represents hydrogen

[0187] R_2 represents hydrogen

[0188] R represents the methacrylate group

[0189] R' represents the methyl radical

[0190] with $(m+n+p)q=113$.

[0191] Test N° 9:

[0192] This test, illustrating the invention, used 0.6% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.97 and consisting of:

[0193] a) 3.2% by weight methacrylic acid as an anionic monomer with a monocarboxylic function

[0194] b) 13.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0195] c) 83.3% by weight of a monomer of formula (I) in which

[0196] R_1 represents hydrogen

[0197] R_2 represents hydrogen

[0198] R represents the methacrylate group

[0199] R' represents the methyl radical

[0200] with $(m+n+p)q=45$.

[0201] Test N° 10:

[0202] This test, illustrating the invention, used 0.6% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.96 and consisting of:

[0203] a) 8.5% by weight methacrylic acid as an anionic monomer with a monocarboxylic function

[0204] b) 13.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0205] c) 78.0% by weight of a monomer of formula (I) in which

[0206] R_1 represents hydrogen

[0207] R_2 represents hydrogen

[0208] R represents the methacrylate group

[0209] R' represents the methyl radical

[0210] with $(m+n+p)q=17$.

[0211] Test N° 11:

[0212] This test, illustrating the invention, used 0.6% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.07 and consisting of:

[0213] a) 17.0% by weight methacrylic acid as an anionic monomer with a monocarboxylic function

[0214] b) 83.0% by weight of a monomer of formula (I) in which

[0215] R_1 represents hydrogen

[0216] R_2 represents hydrogen

[0217] R represents the methacrylate group

[0218] R' represents the methyl radical

[0219] with $(m+n+p)q=45$.

[0220] Test N° 12:

[0221] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.04 and consisting of:

[0222] a) 3.2% by weight methacrylic acid and 13.0% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0223] b) 8.0% by weight acrylamido methyl propanesulphonic acid as an anionic monomer with a sulphonic function

[0224] c) 75.8% by weight of a monomer of formula (I) in which

[0225] R_1 represents hydrogen

[0226] R_2 represents hydrogen

[0227] R represents the methacrylate group

[0228] R' represents the methyl radical

[0229] with $(m+n+p)q=45$.

[0230] Test N° 13:

[0231] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.47 and consisting of:

[0232] a) 3.3% by weight methacrylic acid and 13.0% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0233] b) 5.0% by weight itaconic acid as an anionic monomer with a dicarboxylic function

[0234] c) 78.7% by weight of a monomer of formula (I) in which

[0235] R_1 represents hydrogen

[0236] R_2 represents hydrogen

[0237] R represents the methacrylate group

[0238] R' represents the methyl radical

[0239] with $(m+n+p)q=45$.

[0240] Test N° 14:

[0241] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.38 and consisting of:

[0242] a) 0.8% by weight methacrylic acid and 79.3% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0243] b) 19.9% by weight of a monomer of formula (I) in which

[0244] R_1 represents hydrogen

[0245] R_2 represents hydrogen

[0246] R represents the methacrylate group

[0247] R' represents the methyl radical

[0248] with $(m+n+p)q=45$.

[0249] Test N° 15:

[0250] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.38 and consisting of:

[0251] a) 0.4% by weight methacrylic acid and 79.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0252] b) 20.0% by weight of a monomer of formula (I) in which

[0253] R_1 represents hydrogen

[0254] R_2 represents hydrogen

[0255] R represents the methacrylate group

[0256] R' represents the methyl radical

[0257] with $(m+n+p)q=113$.

[0258] Test N° 16:

[0259] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.28 and consisting of:

[0260] a) 35.0% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0261] b) 20.0% by weight of a monomer of formula (I) in which

[0262] R_1 represents hydrogen

[0263] R_2 represents hydrogen

[0264] R represents the methacrylurethane group

[0265] R' represents the methyl radical

[0266] c) 45.0% by weight acrylamide

[0267] with $(m+n+p)q=17$.

[0268] Test N° 17:

[0269] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.03 and consisting of:

[0270] a) 35.0% by weight acrylic acid as an anionic monomer with a monocarboxylic function

[0271] b) 20.0% by weight of a monomer of formula (I) in which

[0272] R_1 represents hydrogen

[0273] R_2 represents hydrogen

[0274] R represents the methacrylate group

[0275] R' represents the methyl radical

[0276] c) 45.0% by weight acrylamide

[0277] with $(m+n+p)q=45$.

[0278] Test N° 18:

[0279] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.65 and consisting of:

[0280] a) 15.0% by weight methacrylic acid and 12.0% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0281] b) 73.0% by weight of a monomer of formula (I) in which

[0282] R_1 represents hydrogen

[0283] R_2 represents hydrogen

[0284] R represents the methacrylate group

[0285] R' represents the methyl radical

[0286] with $(m+n+p)q=8$.

[0287] Test N° 19:

[0288] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.38 and consisting of:

[0289] a) 3.4% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0290] b) 82.1% by weight of a monomer of formula (I) in which

[0291] R_1 represents hydrogen

[0292] R_2 represents hydrogen

[0293] R represents the methacrylate group

[0294] R' represents the methyl radical

[0295] c) 1.0% by weight EDMA as a cross-linking monomer

[0296] with $(m+n+p)q=45$.

[0297] Test N° 20:

[0298] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.16 and consisting of:

[0299] a) 3.9% by weight methacrylic acid and 1.1% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0300] b) 95.0% by weight of a monomer of formula (I) in which

[0301] R_1 represents hydrogen

[0302] R_2 represents hydrogen

[0303] R represents the methacrylate group

[0304] R' represents the methyl radical

[0305] with $(m+n+p)q=45$.

[0306] Test N° 21:

[0307] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.07 and consisting of:

[0308] a) 0.8% by weight methacrylic acid and 79.2% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0309] b) 20.0% by weight of a monomer of formula (I) in which

[0310] R_1 represents hydrogen

[0311] R_2 represents hydrogen

[0312] R represents the methacrylate group

[0313] R' represents the methyl radical

[0314] with $(m+n+p)q=45$.

[0315] Test N° 22:

[0316] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.28 and consisting of:

[0317] a) 1.7% by weight methacrylic acid and 13.2% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0318] b) 85.6% by weight of a monomer of formula (I) in which

[0319] R₁ represents hydrogen

[0320] R₂ represents hydrogen

[0321] R represents the methacrylate group

[0322] R' represents the propyl radical

[0323] with $(m+n+p)q=64$.

[0324] Test N° 22 bis:

[0325] This test, illustrating the invention, used 0.7% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.68 and consisting of:

[0326] a) 45% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0327] b) 35% by weight acrylamido methyl propanesulphonic acid as an anionic monomer with a sulphonic function

[0328] c) 20% by weight of 2 monomer of formula (I) in which

[0329] R₁ represents hydrogen

[0330] R₂ represents hydrogen

[0331] R represents the methacrylate group

[0332] R' represents the methyl radical

[0333] with $(m+n+p)q=17$.

[0334] All the experimental results are set out in the following Tables 1a to 1d.

TABLE 1a

				BROOKFIELD™ VISCOSITY (mPa · s)						
TEST N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA POTENTIAL (mV)	
			0 rev/min	100 rev/min	0 rev/min	100 rev/min	0 rev/min	100 rev/min		
Prior art	1	100% AA	4.80	1000	280	6000	1500	1000	300	−50.6
Prior art	2	70% AA								
		30% Maleic anhydride	1.38	180	110	2000	500	400	150	−50.7
Field outside invention	3	100% methoxy PEGM 2000	0.91	2400	1600	Excessively high non-measurable viscosity				
Invention	4	8.0% AA	1.28	4680	830	2000	600	1000	440	−20.2
		5.5% EGMP								
		82.0% methoxy PEG MU 5000								
		4.5% EA								
Invention	5	8.0% AA	0.78	3960	1044	7600	960	4000	840	−16.8
		5.5% EGMP								
		75.0% methoxy PEG MU 1800								
		11.5% EA								
Invention	6	8.0% AA								
		5.5% EGMP								
		71.0% methoxy PEG MU 1100	0.51	1860	455	3200	1140	1450	520	−20.7
		15.5% EA								

AA = Acrylic acid.

EA = Ethyl acrylate.

Methoxy PEG MU 1100 = Methoxy polyethylene glycol methacrylurethane with molecular weight 1100.

Methoxy PEGM 2000 = Methoxy polyethylene glycol methacrylate with molecular weight 2000.

EGMP = Ethylene glycol methacrylate phosphate.

Methoxy PEG MU 1800 = Methoxy polyethylene glycol methacrylurethane with molecular weight 1800.

AMPS = Acrylamido-methyl-propane-sulphonic acid.

Methoxy PEG MU 5000 = Methoxy polyethylene glycol methacrylurethane with molecular weight 5000.

[0335]

TABLE 1b

BROOKFIELD™ VISCOSITY (mPa · s)											
TEST N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA POTENTIAL (mV)		
			10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min			
Invention	7	8.0% AA 5.5% EGMP 67.0% methoxy PEG MU 750 19.5% EA	0.51	7600	968	9300	1500	7300	1540	-23.3	
Invention	8	2.0% MAA 13.0% EGMP 85.0% methoxy PEGM 5000	1.56	1800	500	3200	800	1300	450	-7.3	
Invention	9	3.2% MAA 13.5% EGMP 83.3% methoxy PEGM 2000	0.97	750	330	3000	500	700	240	-12.6	
Invention	10	8.5% MAA 13.5% EGMP 78.0% methoxy PEGM 750	0.96	1200	280	5600	920	1700	370	-25.2	
Invention	11	17.0% MAA 83.0% methoxy PEGM 2000	1.07	1700	550	1360	750	1980	650	-16.5	
Invention	12	3.2% MAA 13.0% AA 8.0% AMPS 75.8% methoxy PEGM 2000	1.04	2800	790	3000	900	2100	530	-18.7	

AA = Acrylic acid.

EA = Ethyl acrylate.

MAA = Methacrylic acid.

Methoxy PEG MU 750 = Methoxy polyethylene glycol methacrylurethane with molecular weight 750.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

EGMP = Ethylene glycol methacrylate phosphate.

AMPS = Acrylamido-methyl-propane-sulphonic acid.

Methoxy PEGM 5000 = Methoxy polyethylene glycol methacrylate with molecular weight 5000.

[0336]

TABLE 1c

				BROOKFIELD™ VISCOSITY (mPa · s)						
	TEST			INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA
	N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	POTENTIAL (mV)
Invention	13	3.3% MMA 13.0% AA 5.0% ITCA 78.7% methoxy PEGM 2000	1.47	1100	330	6000	1000	1900	570	−10.9
Invention	14	0.8% MMA 79.3% AA 19.9% methoxy PEGM 2000	1.38	7000	1000	8000	1100	6000	810	−27.5
Invention	15	0.4% MMA 79.6% AA 20.0% methoxy PEGM 5000	1.38	6800	900	8000	1080	5600	800	−24.5
Invention	16	35.0% AA 20.0% methoxy PEG MU 750 45.0% Acrylamide	1.28	7400	1020	9100	1340	7240	1040	−29.8
Invention	17	35.0% AA 20.0% methoxy PEGM 2000 45.0% Acrylamide	1.03	8000	1060	11800	1630	7500	1080	−25.7

TABLE 1c-continued

TEST N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	BROOKFIELD™ VISCOSITY (mPa · s)								ZETA POTENTIAL (mV)
			INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING				
			10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min			
Invention	18	15.0% MMA 12.0% AA 73.0% methoxy PEGM 350	1.65	2200	650	7000	1150	1600	380	−29.8	

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEG MU 750 = Methoxy polyethylene glycol methacrylurethane with molecular weight 750.

Methoxy PEGM 2000 = Methoxy polyethylene glycol methacrylurethane with molecular weight 2000.

Methoxy PEGM 350 = Methoxy polyethylene glycol methacrylate with molecular weight 350.

ITCA = Itaconic acid.

AMPS = Acrylamido-methyl-propane-sulphonic acid.

Methoxy PEGM 5000 = Methoxy polyethylene glycol methacrylate with molecular weight 5000.

[0337]

TABLE 1d

	TEST N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	BROOKFIELD TM VISCOSITY (mPa · s)						ZETA POTENTIAL (mV)
				INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	
Invention	19	3.4% MMA 13.5% AA 82.1% methoxy PEGM 2000 1.0% EDMA	1.38	3400	650	12000	2000	2100	520	−12.5
Invention	20	3.9% MMA 1.1% AA 95.0% methoxy PEGM 2000	1.16	9000	3600	11000	4250	5150	2000	−12.5
Invention	21	0.8% MMA 79.2% AA 20.0% methoxy PEGM 2000	1.07	9400	1080	9000	1250	8050	1150	−20.3
Invention	22	1.7% MMA 13.2% AA 85.6% propoxy PEGM 2800	1.28	11200	1440	12000	2100	9000	1200	−16.5
Invention	22 bis	45% AA 35% AMPS 20% methoxy PEGM 750	0.68	3450	685	3880	1156	3100	653	−28

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol methacrylate with molecular weight 2000.

Propoxy PEGM 2800 = Propoxy polyethylene glycol methacrylate with molecular weight 2800.

Methoxy PEGM 750 = Methoxy polyethylene glycol methacrylate with molecular weight 750

AMPS = Acrylamido-methyl-propane-sulphonic acid

[0338] A reading of Tables 1a to 1d shows that the use of copolymer according to the invention containing, as a non-ionic monomer, at least one monomer of formula (I) results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a moderate to high mineral material content, stable over time and having a low Zeta potential.

EXAMPLE 2

[0339] The purpose of this example is to illustrate different levels of use of dispersing agent according to the invention.

[0340] To this end, with the same operating method and the same equipment as in example 1, different levels of copolymer according to the invention are tested.

[0341] Test N° 23:

[0342] This test, illustrating the invention, used 0.4% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.98 and consisting of:

[0343] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0344] b) 83.0% by weight of a monomer of formula (I) in which

[0345] R₁ represents hydrogen

[0346] R₂ represents hydrogen

[0347] R represents the methacrylate group

[0348] R' represents the methyl radical

[0349] with (m+n+p)q=45.

[0359] Test N° 25:

[0360] This test, illustrating the invention, used 1.0% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.86 and consisting of:

[0361] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0362] b) 83.0% by weight of a monomer of formula (I) in which

[0363] R₁ represents hydrogen

[0364] R₂ represents hydrogen

[0365] R represents the methacrylate group

[0366] R' represents the methyl radical

[0367] with (m+n+p)q=17.

[0368] All the experimental results are set out in Table 2 below.

TABLE 2

	TEST N°	CONSTITUENT MONOMERS	QUANTITY OF AGENT (% dry/dry)	BROOKFIELD™ VISCOSITY (mPa · s)						ZETA POTENTIAL (mV)
				INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	
Invention	23	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	0.4	2000	480	1800	660	1890	540	−20.8
Invention	24	3.5% MMA 13.5% AA 83.0% methoxy PEGM 500	0.6	2600	540	3000	750	2500	510	−24.2
Invention	25	3.5% MMA 13.5% AA 83.0% methoxy PEGM 750	1.0	8000	1300	9000	1600	8500	1500	−25.9

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 750 = Methoxy polyethylene glycol methacrylate with molecular weight 750.

Methoxy PEGM 2000 = Methoxy polyethylene glycol methacrylate with molecular weight 2000.

Methoxy PEGM 500 = Methoxy polyethylene glycol methacrylate with molecular weight 500.

[0350] Test N° 24:

[0351] This test, illustrating the invention, used 0.6% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.17 and consisting of:

[0352] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0353] b) 83.0% by weight of a monomer of formula (I) in which

[0354] R₁ represents hydrogen

[0355] R₂ represents hydrogen

[0356] R represents the methacrylate group

[0357] R' represents the methyl radical

[0358] with (m+n+p)q=11.

[0369] A reading of Table 2 shows that the aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a moderate to high mineral material content, stable over time and having a low Zeta potential, contain 0.05% to 5% by dry weight of the agent according to the invention compared with the total dry weight of the fillers and/or pigments, and even more particularly 0.3% to 1.0% by dry weight of the said agent with respect to the total dry weight of the fillers and/or pigments.

EXAMPLE 3

[0370] The purpose of this example is to illustrate the different values of the product (m+n+p)q of the monomer with an unsaturated ethylenic non-ionic chain of formula (I) of the dispersing agent according to the invention.

[0371] For this purpose, with the same operating mode and the same equipment as in example 1, different copolymers according to the invention are tested.

[0372] Test N° 26:

[0373] This test, illustrating the invention, used 0.4% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.19 and consisting of:

[0374] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0375] b) 83.0% by weight of a monomer of formula (I) in which

[0376] R_1 represents hydrogen

[0377] R_2 represents hydrogen

[0378] R represents the methacrylate group

[0379] R' represents the methyl radical

[0380] with $(m+n+p)q=17$.

[0381] Test N° 27:

[0382] This test, illustrating the invention, used 0.8% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 0.81 and consisting of:

[0383] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0384] b) 83.0% by weight of a monomer of formula (I) in which

[0385] R_1 represents hydrogen

[0386] R_2 represents hydrogen

[0387] R represents the methacrylate group

[0388] R' represents the methyl radical

[0389] with $(m+n+p)q=25$.

[0390] Test N° 28:

[0391] This test, illustrating the invention, used 0.4% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 1.05 and consisting of:

[0392] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0393] b) 83.0% by weight of a monomer of formula (T) in which

[0394] R_1 represents hydrogen

[0395] R_2 represents hydrogen

[0396] R represents the methacrylate group

[0397] R' represents the methyl radical

[0398] with $(m+n+p)q=45$.

[0399] Test N° 29:

[0400] This test, illustrating the invention, used 0.4% by dry weight of a polymer fully neutralised with soda, with a specific viscosity of 2.57 and consisting of:

[0401] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0402] b) 83.0% by weight of a monomer of formula (I) in which

[0403] R_1 represents hydrogen

[0404] R_2 represents hydrogen

[0405] R represents the methacrylate group

[0406] R' represents the methyl radical

[0407] with $(m+n+p)q=113$.

[0408] All the experimental results are set out in Table 3 below.

TABLE 3

				BROOKFIELD™ VISCOSITY (mPa · s)							
				INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA	
	TEST N°	CONSTITUENT MONOMERS	(m + n + p)q	10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	POTENTIAL (mV)	
Invention	26	3.5% MMA 13.5% AA 83.0% methoxy PEGM 750	17	4000	820	3200	980	4500	930	-23.9	
Invention	27	3.5% MMA 13.5% AA 83.0% methoxy PEGM 1100	25	3200	810	4000	1000	3500	940	-22.1	
Invention	28	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	45	2000	470	3000	850	2230	590	-18.6	
Invention	29	3.5% MMA 13.5% AA 83.0% methoxy PEGM 5000	113	4600	820	9000	1600	5000	1200	-6.7	

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 750 = Methoxy polyethyleneglycolmethacrylate with molecular weight 750.

Methoxy PEGM 2000 = Methoxy polyethyleneglycolmethacrylate with molecular weight 2000.

Methoxy PEGM 1100 = Methoxy polyethyleneglycolmethacrylate with molecular weight 1100.

Methoxy PEGM 5000 = Methoxy polyethyleneglycolmethacrylate with molecular weight 5000.

[0409] A reading of Table 3 shows that the use of a copolymer according to the invention containing, as a non-ionic monomer, at least one monomer of formula (I) with $5 \leq (m+n+p)q \leq 150$ results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a moderate to high mineral material content, stable over time and having a low Zeta potential.

EXAMPLE 4

[0410] The purpose of this example is to illustrate different molecular weights of the dispersing agent according to the invention.

[0411] For this purpose, with the same operating mode and the same equipment as in example 1, tests were carried out on different copolymers which all had a different specific viscosity for the same composition by weight of monomer and the same form of neutralisation.

[0412] For tests 30 to 35, these were copolymers fully neutralised with soda and consisting of

[0413] a) 3.2% by weight methacrylic acid as an anionic monomer with a monocarboxylic function

[0414] b) 13.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0415] c) 83.3% by weight of a monomer of formula (I) in which:

[0416] R_1 represents hydrogen

[0417] R_2 represents hydrogen

[0418] R represents the methacrylate group

[0419] R' represents the methyl radical

[0420] with $(m+n+p)q=45$.

[0421] and having the following specific viscosities:

[0422] Test N° 30:

[0423] The polymer used in this test, at 0.6% by dry weight with respect to the dry weight of marble, has a specific viscosity of 0.97 and illustrates the invention.

[0424] Test N° 31:

[0425] The polymer used in this test, at 0.6% by dry weight with respect to the dry weight of marble, has a specific viscosity of 1.57 and illustrates the invention.

[0426] Test N° 32:

[0427] The polymer used in this test, at 1.0% by dry weight with respect to the dry weight of marble, has a specific viscosity of 1.75 and illustrates the invention.

[0428] Test N° 33:

[0429] The polymer used in this test, at 0.8% by dry weight with respect to the dry weight of marble, has a specific viscosity of 3.72 and illustrates the invention.

[0430] Test N° 34:

[0431] The polymer used in this test, at 1.0% by dry weight with respect to the dry weight of marble, has a specific viscosity of 3.74 and illustrates the invention.

[0432] Test N° 35:

[0433] The polymer used in this test, at 1.0% by dry weight with respect to the dry weight of marble, has a specific viscosity of 5.08 and illustrates the invention.

[0434] For tests 36 to 39, these are copolymers fully neutralised with soda and consisting of

[0435] a) 8.0% by weight acrylic acid as an anionic monomer with a monocarboxylic function

[0436] b) 5.5% by weight ethylene glycol methacrylate phosphate as an anionic monomer with a phosphoric function

[0437] c) 82.0% by weight of a monomer of formula (I) in which:

[0438] R_1 represents hydrogen

[0439] R_2 represents hydrogen

[0440] R represents the methacrylurethane group

[0441] R' represents the methyl radical

[0442] d) 4.5% by weight ethyl acrylate

[0443] with $(m+n+p)q=113$.

[0444] and having the following specific viscosities:

[0445] Test N° 36:

[0446] The polymer used in this test, at 0.8% by dry weight with respect to the dry weight of marble, has a specific viscosity of 1.19 and illustrates the invention.

[0447] Test N° 37:

[0448] The polymer used in this test, at 0.8% by dry weight with respect to the dry weight of marble, has a specific viscosity of 1.31 and illustrates the invention.

[0449] Test N° 38:

[0450] The polymer used in this test, at 0.8% by dry weight with respect to the dry weight of marble, has a specific viscosity of 1.83 and illustrates the invention.

[0451] Test N° 39:

[0452] The polymer used in this test, at 0.8% by dry weight with respect to the dry weight of marble, has a specific viscosity of 2.04 and illustrates the invention.

[0453] For tests 40 and 41, these are copolymers fully neutralised with soda and consisting of

[0454] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0455] b) 83.0% by weight of a monomer of formula (I) in which:

[0456] R_1 represents hydrogen

[0457] R_2 represents hydrogen

[0458] R represents the methacrylate group

[0459] R' represents the methyl radical

[0460] with (m+n+p)_q 45.

[0461] and having the following specific viscosities:

[0462] Test N° 40:

[0463] The polymer used in this test, at 0.4% by dry weight with respect to the dry weight of marble, has a specific viscosity of 0.98 and illustrates the invention.

[0464] Test N° 41:

[0465] The polymer used in this test, at 0.4% by dry weight with respect to the dry weight of marble, has a specific viscosity of 2.33 and illustrates the invention.

[0466] All the Brookfield™ viscosity and Zeta potential experimental results measured with the same equipment and under the same operating conditions as in Example 1 are set out in Tables 4a and 4b below.

TABLE 4a

				BROOKFIELD™ VISCOSITY (mPa · s)						
TEST N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA POTENTIAL (mV)	
			10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min		
Invention	30	3.2% MMA 13.5% EGMP 83.3% methoxy PEGM 2000	0.97	750	330	3000	500	700	240	−12.6
Invention	31	3.2% MMA 13.5% EGMP 83.3% methoxy PEGM 2000	1.57	7400	920	13000	1300	8400	1120	−15.7
Invention	32	3.2% MMA 13.5% EGMP 83.3% methoxy PEGM 2000	1.75	19000	2900	22000	3200	20000	3000	−16.8
Invention	33	3.2% MMA 13.5% EGMP 83.3% methoxy PEGM 2000	3.72	20000	2800	25000	3000	22000	2900	−16
Invention	34	3.2% MMA 13.5% EGMP 83.3% methoxy PEGM 2000	3.74	9000	1450	13000	1950	10000	1550	−15.7
Invention	35	3.2% MMA 13.5% EGMP 83.3% methoxy PEGM 2000	5.08	13000	2600	15000	2750	14000	2700	−18.6

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

EGMP = Ethylene glycol methacrylate phosphate.

EA = Ethyl acrylate.

[0467]

TABLE 4b

				BROOKFIELD™ VISCOSITY (mPa · s)						
	TEST N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA POTENTIAL (mV)
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	
Invention	36	8.0% AA 5.5% EGMP 82.0% methoxy PEG MU 5000 4.5% EA	1.19	2200	780	5000	1700	3200	1140	−6.2
Invention	37	8.0% AA 5.5% EGMP 82.0% methoxy PEG MU 5000 4.5% EA	1.31	950	430	4500	700	700	390	−5.7
Invention	38	8.0% AA 5.5% EGMP 82.0% methoxy PEG MU 5000 4.5% EA	1.83	6400	970	7000	1100	1900	600	−8.6

TABLE 4b-continued

				BROOKFIELD™ VISCOSITY (mPa · s)						
	TEST N°	CONSTITUENT MONOMERS	SPECIFIC VISCOSITY	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	POTENTIAL (mV)
Invention	39	8.0% AA 5.5% EGMP 82.0% methoxy PEG MU 5000 4.5% EA	2.04	6800	1280	9000	1350	2200	920	−5.6
Invention	40	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	0.98	2000	480	1800	660	1890	540	−20.8
Invention	41	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	2.33	6400	920	5000	1010	6900	1400	−15.2

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

EGMP = Ethylene glycol methacrylate phosphate.

Methoxy PEG MU 5000 = Methoxy polyethylene glycol methacrylurethane with molecular weight 5000.

EA = Ethyl acrylate.

[0468] A reading of Tables 4a and 4b shows that the use of a copolymer according to the invention having a specific viscosity of no more than 10, preferentially no more than 5 and highly preferentially no more than 2, results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a high mineral material content, stable over time and having a low Zeta potential.

EXAMPLE 5

[0469] The purpose of this example is to illustrate different types and degrees of neutralisation of the dispersing agent according to the invention.

[0470] For this purpose, with the same operating mode and the same equipment as in example 1, tests were carried out, at 0.4% by dry weight with respect to the dry weight of marble, on the following different copolymers, which had different neutralisations for the same composition by weight of monomer and the same specific viscosity.

[0471] These were all copolymers with a specific viscosity of 1.05 and consisting of:

[0472] a) 3.5% by weight methacrylic acid and 13.5% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0473] b) 83.0% by weight of a monomer of formula (I) in which:

[0474] R₁ represents hydrogen

[0475] R₂ represents hydrogen

[0476] R represents the methacrylate group

[0477] R' represents the methyl radical

[0478] with (m+n+p)q=45.

[0479] The different types and degrees of neutralisation are as follows:

[0480] Test N° 42:

[0481] The polymer used in this test is fully neutralised with potash and illustrates the invention.

[0482] Test N° 43:

[0483] The polymer used in this test is fully neutralised with ammonium hydroxide and illustrates the invention.

[0484] Test N° 44:

[0485] The polymer used in this test is totally acidic and illustrates the invention.

[0486] Test N° 45:

[0487] The polymer used in this test is fully neutralised with triethanolamine and illustrates the invention.

[0488] Test N° 46:

[0489] The polymer used in this test is fully neutralised with lithium hydroxide and illustrates the invention.

[0490] Test N° 47:

[0491] The polymer used in this test is neutralised to the extent of 50% molar with magnesium hydroxide and illustrates the invention.

[0492] Test N° 48:

[0493] The polymer used in this test is fully neutralised with a mixture composed of 70% molar soda and 30% molar lime and illustrates the invention.

[0494] Test No 49:

[0495] The polymer used in this test is fully neutralised with a mixture composed of 50% molar soda and 50% molar magnesium hydroxide and illustrates the invention.

[0496] All the Brookfield™ viscosity and Zeta potential experimental results measured with the same equipment and

under the same operating conditions as in Example 1 are set out in Tables 5a and 5b below.

TABLE 5a

				BROOKFIELD™ VISCOSITY (mPa · s)						
	TEST N°	CONSTITUENT MONOMERS	NEUTRALI-SATION	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	POTENTIAL (mV)
Invention	42	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	100 K	1100	255	3000	700	1200	290	−19.5
Invention	43	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	100 NH ₄ OH	6000	840	6000	1100	4500	790	−14.7
Invention	44	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	0	2200	490	5000	1000	2500	290	−10.1
Invention	45	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	100 TEA	4500	700	4000	900	2900	550	−14.8
Invention	46	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	100 Li	4100	670	8000	1050	7000	950	−20.3
Invention	47	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	50 Mg	1500	360	3500	650	1700	325	−8.8

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

[0497]

TABLE 5b

				BROOKFIELD™ VISCOSITY (mPa · s)						
	TEST N°	CONSTITUENT MONOMERS	NEUTRALI-SATION	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	POTENTIAL (mV)
Invention	48	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	70 Na–30 Ca	4000	620	5000	1000	4000	720	–18.9
Invention	49	3.5% MMA 13.5% AA 83.0% methoxy PEGM 2000	50 Na–50 Mg	4600	800	7000	1100	5200	850	–15.5

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

[0498] A reading of Tables 5a and 5b shows that the use of a copolymer according to the invention, totally acid or partially or totally neutralised with one or more neutralisation agents having a monovalent neutralising function or a polyvalent neutralising function results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a high mineral matter content, stable over time and having a low Zeta potential.

EXAMPLE 6

[0499] This example relates to the grinding of a suspension of natural calcium carbonate in order to refine into a microparticulate suspension.

[0500] For this purpose, for each test, 0.75% by dry weight, with respect to the total dry weight of the calcium carbonate, of grinding aid agent to be tested, was introduced

into an aqueous suspension of 42% dry matter of a marble coming from the Carrara deposits and with a mean diameter of around 10 μm .

[0501] The suspension circulated in a grinder of the Dyno-Mill type with a fixed cylinder and rotating impeller, whose grinding substance consisted of corundum balls with a diameter in the range from 0.6 millimetres to 1 millimetre.

[0502] The total volume occupied by the grinding substance was 1150 cubic centimetres whilst its weight was 2900 g.

[0503] The grinding chamber had a volume of 1400 cubic centimetres.

[0504] The circumferential speed of the grinder was 10 metres per second.

[0505] The suspension of calcium carbonate was recycled at the rate of 18 litres per hour.

[0506] The outlet of the Dyno-Mill was provided with a separator with 200 micron mesh for separating the suspension resulting from the grinding and the grinding substance.

[0507] The temperature during each grinding test was kept at approximately 60° C.

[0508] At the end of the grinding (T_0), a sample of the pigmentary solution was recovered in a flask. The granulometry of the suspension (% of particles less than 1 micrometre) was measured by means of a Sedigraph™ 5100 granulometer from Micromeritics.

[0509] The Brookfield™ viscosity of the suspension was measured by means of a Brookfield™ type RVT viscometer, at a temperature of 20° C. and speeds of rotation of 10 revolutions per minute and 100 revolutions per minute with the appropriate spindle.

[0510] After leaving at rest for 8 days in the flask, the Brookfield™ viscosity of the suspension was measured by introducing, into the unstirred flask, the appropriate spindle of the Brookfield™ type RVT viscometer, at a temperature of 20° C. and speeds of rotation of 10 revolutions per minute and 100 revolutions per minute (viscosity BS=before stirring).

[0511] The same Brookfield™ viscosity measurements were also carried out once the flask was stirred and constituted the AS (after stirring) viscosity results.

[0512] Thus, in the different tests the following different grinding aid agents were tested.

[0513] Test N° 50:

[0514] This test, illustrating the invention, uses a polymer 100% neutralised with soda, with a specific viscosity of 0.98 and consisting of:

[0515] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0516] b) 83.0% by weight of a monomer of formula (I) in which

[0517] R_1 represents hydrogen

[0518] R_2 represents hydrogen

[0519] R represents the methacrylate group

[0520] R' represents the methyl radical

[0521] with $(m+n+p)q=45$.

[0522] Test N° 51:

[0523] This test, illustrating the invention, uses a polymer fully neutralised with potash, with a specific viscosity of 0.98 and consisting of:

[0524] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0525] b) 83.0% by weight of a monomer of formula (I) in which

[0526] R_1 represents hydrogen

[0527] R_2 represents hydrogen

[0528] R represents the methacrylate group

[0529] R' represents the methyl radical

[0530] with $(m+n+p)q=45$.

[0531] Test N° 52:

[0532] This test, illustrating the invention, uses a polymer, with a specific viscosity of 0.98, fully neutralised so that 50% of the acid groups are neutralised with soda and 50% of the acid groups are neutralised with magnesium hydroxide, and consisting of:

[0533] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0534] b) 83.0% by weight of a monomer of formula (I) in which

[0535] R_1 represents hydrogen

[0536] R_2 represents hydrogen

[0537] R represents the methacrylate group

[0538] R' represents the methyl radical

[0539] with $(m+n+p)q=45$.

[0540] Test N° 53:

[0541] This test, illustrating the invention, uses a non-neutralised polymer, with a specific viscosity of 0.98 and consisting of:

[0542] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0543] b) 83.0% by weight of a monomer of formula (I) in which

[0544] R_1 represents hydrogen

[0545] R_2 represents hydrogen

[0546] R represents the methacrylate group

[0547] R' represents the methyl radical

[0548] with $(m+n+p)q=45$.

[0549] All the Brookfield™ viscosity and Zeta potential experimental results measured with the same equipment and

under the same operating conditions as in Example 1 are set out in Table 6 below.

[0556] The circumferential speed of the grinder was 10 metres per second.

TABLE 6

BROOKFIELD™ VISCOSITY (mPa · s)												
		DEGREE OF		GRANU-		INITIAL		8 days BEFORE		8 days AFTER		ZETA
	TEST	CONSTITUENT	NEUTRALISA-	LOMETRY	10	100	10	100	10	100	POTENTIAL	
	N°	MONOMERS	TION/ION	(% <1 μm)	rev/min	rev/min	rev/min	rev/min	rev/min	rev/min	(mV)	
Invention	50	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	100 Na	70.4	2400	370	1700	455	750	170	-15.7	
Invention	51	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	100 K	73.9	2550	430	1500	535	950	230	-13.4	
Invention	52	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	50 Na-50 Mg	72.3	1300	300	650	120	650	112	-11.9	
Invention	53	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	0	70.7	2850	460	1350	315	500	93	-8.7	

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

[0550] A reading of Table 6 shows that the use of a copolymer according to the invention, totally acidic or partially or totally neutralised with one or more neutralisation agents having a monovalent neutralisation function or a polyvalent neutralisation function results in the obtaining of aqueous solutions of ground mineral pigments and/or fillers, according to the invention, with a moderate to high mineral material content, stable over time and having a low Zeta potential.

EXAMPLE 7

[0551] This example relates to the grinding of a suspension of dolomite in order to refine it into a microparticulate suspension.

[0552] For this purpose, for each test, a grinding aid agent to be tested was introduced, to the extent of 0.5% by dry weight, with respect to the total dry weight of dolomite, into an aqueous suspension with 65% dry matter of a dolomite whose 4.2% are not passing through a 100 μ m sieve and whose median diameter measured by means of a CILAS type 850 granulometer was 15.03 micrometres.

[0553] The suspension circulated in a grinder of the Dyno-Mill type with fixed cylinder and rotating impeller, whose grinding substance consisted of balls of corundum with a diameter in the range 0.6 millimetres to 1 millimetre.

[0554] The total volume occupied by the grinding substance was 1150 cubic centimetres whilst its weight was 2900 g.

[0555] The grinding chamber had a volume of 1400 cubic centimetres.

[0557] The suspension of dolomite was recycled at 18 litres per hour.

[0558] The outlet from the Dyno-Mill was provided with a separator with meshes of 200 microns for separating the suspension resulting from the grinding, and the grinding substance.

[0559] The temperature during each grinding test was maintained at approximately 60° C.

[0560] At the end of grinding (T_0), a sample of the pigmentary suspension was recovered in a flask. The granulometry of the suspension (% of particles less than 2 micrometres) was measured by means of a CILAS type 850 granulometer.

[0561] The Brookfield™ viscosity of the suspension was measured by means of a Brookfield™ type RVT viscometer, at a temperature of 20° C. and speeds of rotation of 10 revolutions per minute and 100 revolutions per minute with the appropriate spindle.

[0562] After a residence time of 8 days in the flask, the Brookfield™ viscosity of the suspension was measured by introducing, into the unstirred flask, the appropriate spindle of the Brookfield™ type RVT viscometer, at a temperature of 20° C. and speeds of rotation of 10 revolutions per minute and 100 revolutions per minute (viscosity BS=before stirring).

[0563] The same Brookfield™ viscosity measurements were also made once the flask had been stirred and constitute the AS (after stirring) viscosity results.

[0564] Thus, in the different tests, the following different grinding aid agents were tested.

[0565] Test N° 54:

[0566] This test, illustrating the invention, uses a non-neutralised polymer, with a specific viscosity of 0.98 and consisting of:

[0567] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0568] b) 83.0% by weight of a monomer of formula (I) in which

[0569] R_1 represents hydrogen

[0570] R_2 represents hydrogen

[0571] R represents the methacrylate group

[0572] R' represents the methyl radical

[0573] with $(m+n+p)q=45$.

[0574] Test N° 55:

[0575] This test, illustrating the invention, uses a polymer fully neutralised with soda, with a specific viscosity of 0.98 and consisting of:

[0576] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0583] Test N° 56:

[0584] This test, illustrating the invention, uses a polymer fully neutralised with potash, with a specific viscosity of 0.98 and consisting of:

[0585] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0586] b) 83.0% by weight of a monomer of formula (I) in which

[0587] R_1 represents hydrogen

[0588] R_2 represents hydrogen

[0589] R represents the methacrylate group

[0590] R' represents the methyl radical

[0591] with $(m+n+p)q=45$.

[0592] All the Brookfield™ viscosity and Zeta potential experimental results measured with the same equipment and under the same operating conditions as in Example 1 are set out in Table 7 below.

TABLE 7

					BROOKFIELD™ VISCOSITY (mPa · s)						
			DEGREE OF	GRANU-	INITIAL		8 days BEFORE		8 days AFTER		ZETA
	TEST N°	CONSTITUENT MONOMERS	NEUTRALISA-TION/ION	LOMETRY (% <2 μm)	10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	POTENTIAL (mV)
Invention	54	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	0	50.4	1070	183	1940	274	1330	205	-5.7
Invention	55	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	100 Na	56.6	2070	266	2300	305	1910	261	-7.0
Invention	56	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	100 K	52.1	2570	341	3470	436	3460	439	-8.2

MAA = Methacrylic acid.

AA = Acrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

[0577] b) 83.0% by weight of a monomer of formula (I) in which

[0578] R_1 represents hydrogen

[0579] R_2 represents hydrogen

[0580] R represents the methacrylate group

[0581] R' represents the methyl radical

[0582] with $(m+n+p)q=45$.

[0593] A reading of Table 7 shows that the use of a copolymer according to the invention results in the obtaining of aqueous suspensions of ground dolomites, according to the invention, with a moderate to high mineral material content, stable over time and having a low Zeta potential.

EXAMPLE 8

[0594] This example relates to the grinding of a suspension of natural calcium carbonate in order to refine it into a

microparticulate suspension in an industrial microelement grinder, followed by a reconcentration and a dispersal of the concentrated suspension by means of the dispersing agent according to the invention.

[0595] For this purpose, for each test according to the invention (Tests 57 and 58), after a grinding of an aqueous suspension with 41% dry matter of a Norwegian marble, using 0.6% by dry weight, with respect to the total dry weight of the calcium carbonate, of a grinding aid agent according to the invention, a polymer neutralised to the extent of 50% molar by potash, with a specific viscosity equal to 0.98 and consisting of:

[0596] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0597] b) 83.0% by weight of a monomer of formula (I) in which

[0598] R_1 represents hydrogen

[0599] R_2 represents hydrogen

[0600] R represents the methacrylate group

[0601] R' represents the methyl radical

[0602] with $(m+n+p)q=45$,

[0603] a thermal reconcentration of the refined suspension obtained was carried out until a slurry was obtained with a dry calcium carbonate concentration of 72%.

[0604] For Test N° 57 illustrating the invention, there was introduced into the thermal concentrator, during the reconcentration step, 0.75% by dry weight, with respect to the dry weight of calcium carbonate, of the copolymer fully neu-

tralised with soda, with a specific viscosity of 0.98 and consisting of:

[0605] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0606] b) 83.0% by weight of a monomer of formula (I) in which

[0607] R_1 represents hydrogen

[0608] R_2 represents hydrogen

[0609] R represents the methacrylate group

[0610] R' represents the methyl radical

[0611] with $(m+n+p)q=45$.

[0612] For Test N° 58 illustrating the invention, there was introduced into the thermal concentrator, during the reconcentration step, 0.75% by dry weight, with respect to the dry weight of calcium carbonate, of the copolymer with a specific viscosity of 0.98, fully neutralised with potash and consisting of:

[0613] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0614] b) 83.0% by weight of a monomer of formula (I) in which

[0615] R_1 represents hydrogen

[0616] R_2 represents hydrogen

[0617] R represents the methacrylate group

[0618] R' represents the methyl radical

[0619] with $(m+n+p)q=45$.

[0620] All the Brookfield™ viscosity, Zeta potential and granulometry experimental results measured with the same equipment and under the same operating conditions as in Example 1 are set out in Table 8 below.

TABLE 8

		DISPERSANT USED IN			BROOKFIELD™ VISCOSITY (mPa · s)						
		RECONCENTRATION		DEGREE OF	GRANU-	8 days BEFORE 8 days AFTER					
						INITIAL		STIRRING		STIRRING	
TEST	N°	CONSTITUENT MONOMERS	NEUTRALISATION/ION	LOMETRY (% <1 µm)	10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min	POTENTIAL (mV)
Invention	57	3.4% MMA 13.6% AA 83.0% methoxy PEGM 2000	100 Na	76.6	2520	942	1100	900	1650	565	-7.2
Invention	58	3.4% MMA 13.6% AA 83.0% methoxy PEGM 200	100 K	75.7	1750	583	1200	690	1320	407	-7.8

AA = Acrylic acid.

MAA = Methacrylic acid.

Methoxy PEGM 2000 = Methoxy polyethylene glycol with molecular weight 2000.

[0621] A reading of Table 8 shows that the use of a copolymer according to the invention results in the obtaining of aqueous suspensions of mineral pigments and/or fillers ground and then reconcentrated, according to the invention, with a moderate to high mineral material content, stable over time and having a low Zeta potential.

EXAMPLE 9

[0622] This example relates to the preparation of a suspension of different mineral fillers by simple dispersion and the revealing of the properties afforded by the presence of at least one monomer of formula (I) in the non-ionic monomer.

[0623] For this purpose, the aqueous suspension of mineral filler to be tested is prepared by the introduction first of all of the agent to be tested into the water and then of the mineral material to be dispersed.

[0624] Test N° 59:

[0625] This test illustrates the invention and uses kaolin (kaolin SPS from ECC) as a mineral material at a dry matter concentration of 60.5% and, as a dispersing agent, 1.0% by dry weight, with respect to the dry weight of kaolin, of a copolymer with a specific viscosity of 0.98, fully neutralised with potash and consisting of:

[0626] a) 3.4% by weight methacrylic acid and 13.6% by weight acrylic acid as anionic monomers with a monocarboxylic function

[0635] Test N° 61:

[0636] This test illustrates the invention and uses, as a mineral material, lime supplied by Aldrich at a dry matter concentration of 60.6% and, as a dispersing agent, 1.0% by dry weight, with respect to the dry weight of lime, of the same copolymer as the one used in Test N° 59.

[0637] Test N° 62:

[0638] This test illustrates the invention and uses, as a mineral material, magnesium hydroxide supplied by Aldrich at a dry matter concentration of 60.5% and, as a dispersing agent, 0.4% by dry weight, with respect to the dry weight of magnesium hydroxide, of the same copolymer as the one used in Test N° 59.

[0639] Test N° 63:

[0640] This test illustrates the invention and uses, as a mineral material, a chalk sold by Omya under the name Etiquette Violette at a dry matter concentration of 70% and, as a dispersing agent, 0.3% by dry weight, with respect to the dry weight of chalk, of the same copolymer as the one used in Test N° 59.

[0641] All the Brookfield™ viscosity and Zeta potential experimental results measured with the same equipment and under the same operating conditions as in Example 1 are set out in Table 9 below.

TABLE 9

			BROOKFIELD™ VISCOSITY (mPa · s)							
TEST N°	MINERAL FILLER	DRY MATTER %	INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING		ZETA POTENTIAL (mV)	
			10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min		
Invention	59	Kaolin	60.5	3830	760	8000	1400	5200	950	−10.6
Invention	60	Titanium dioxide	60.4	2600	480	3000	550	1100	170	−17.2
Invention	61	Chalk	60.6	800	530	20000	4800	10000	4400	−7.6
Invention	62	Magnesium hydroxide	60.5	400	180	3000	3800	200	130	−3.6
Invention	63	Chalk	70	790	146	3880	891	1740	277	−28

[0627] b) 83.0% by weight of a monomer of formula (I) in which

[0628] R₁ represents hydrogen

[0629] R₂ represents hydrogen

[0630] R represents the methacrylate group

[0631] R' represents the methyl radical

[0632] with (m+n+p)q=45.

[0633] Test N° 60:

[0634] This test illustrates the invention and uses, as a mineral material, titanium dioxide sold by Tioxide under the name R-HD2 at a dry matter concentration of 60.4% and, as a dispersing agent, 0.4% in dry weight, with respect to the dry weight of titanium dioxide, of the same copolymer as the one used in Test N° 59.

[0642] A reading of Table 9 shows that the use of a copolymer according to the invention containing, as a non-ionic monomer, at least one monomer of formula (I) results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a moderate to high mineral material content, stable over time and having a low Zeta potential, whatever the mineral material used.

EXAMPLE 10

[0643] The purpose of this example is to illustrate the low sensitivity of the aqueous suspensions according to the invention to alkaline pHs.

[0644] To do this, a quantity of polymer to be tested corresponding to 0.73% by dry weight with respect to the dry weight of mineral material was introduced into water.

[0645] After homogenisation of the polymer in the water by stirring, the pH of the medium was adjusted to 9 by adding soda.

[0658] All the Brookfield™ viscosity and conductivity experimental results are set out in Table 10 below.

TABLE 10

	TEST N°	pH	CONDUCTIVITY mS/cm	BROOKFIELD™ VISCOSITY (mPa · s)					
				INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING	
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min
Prior art	64	7.5	2.27	10000	2764	Viscosity	too	not	measurable
		10	2.7	3460	926	3480	high	3390	858
		13	11.2	50800	7440	Viscosity	994	not	measurable
Invention	65	7.5	1.4	320	252	1020	442	430	300
		10	1.7	400	362	820	531	450	366
		13	4.8	8920	2500	10500	4230	8600	3204

[0646] The pH being constant, the necessary quantity of mineral material for obtaining a dry matter concentration of 70% was then introduced.

[0647] After 30 minutes stirring, ammonium hydroxide was added until a pH of 10 was obtained.

[0648] The sample was then divided into three parts.

[0649] The first part was reserved for a study of the Brookfield™ viscosity carried out with the same operating method and the same equipment as in the previous examples.

[0650] The second part of the sample was stirred for 30 minutes. After these 30 minutes of stirring, the pH was lowered to 7.5 by means of acetic acid.

[0651] At the end of 20 minutes additional stirring, a measurement of conductivity of the aqueous suspension of mineral material was carried out by means of a conductivity meter type LF 320 sold by Wissenschaftliche Technische Werkstätten. This value then corresponded to the conductivity of the suspension at a pH of 7.5. The sample was then subjected to a study of Brookfield™ viscosity as previously described.

[0652] The third part of the sample was stirred for 30 minutes. After these 30 minutes of stirring, the pH was raised to 13 by adding soda.

[0653] At the end of 20 minutes additional stirring, a measurement of conductivity of the aqueous suspension of mineral material was carried out using the same conductivity meter as the one used previously. This value then corresponded to the conductivity of the suspension at a pH of 13. The sample was then subjected to a study of Brookfield™ viscosity as previously described.

[0654] Test N° 64:

[0655] This test illustrates the prior art and uses, as a mineral material, a precipitated calcium carbonate sold by Solvay under the name Socal™ P3 and, as a dispersing agent, a polyacrylic acid with a specific viscosity of 0.84.

[0656] Test N° 65:

[0657] This test illustrates the invention and uses, as a mineral material, a precipitated calcium carbonate sold by Solvay under the name Socal™ P3 and, as a dispersing agent, the same copolymer as the one used in Test N° 59.

[0659] A reading of Table 10 shows that the use of a copolymer according to the invention containing at least one monomer of formula (I) as a non-ionic monomer results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a moderate or high mineral matter content, stable over time and having a low sensitivity to alkaline pHs.

EXAMPLE 11

[0660] The purpose of this example is to illustrate the low sensitivity of the aqueous suspensions according to the invention to acidic or weakly alkaline pHs.

[0661] To do this, a quantity of polymer to be tested corresponding to 0.45% by dry weight with respect to the dry weight of mineral material was introduced into water.

[0662] After homogenisation of the polymer in water by stirring, the necessary quantity of mineral material for obtaining a dry matter concentration of 60% was introduced.

[0663] After 30 minutes stirring, the sample was then divided into three parts for measurements of Brookfield™ viscosity and conductivity on each of the parts of the sample with the same operating method and the same equipment as used in the previous example.

[0664] The first part corresponded to a natural pH of a dispersion of 8 and was reserved for the study of Brookfield™ viscosity as described in Example 10.

[0665] For the second part of the sample, the pH was reduced to 6 by means of hydrochloric acid.

[0666] At the end of 20 minutes additional stirring, a measurement of conductivity of the aqueous suspension of the mineral matter was carried out. This value then corresponded to the conductivity of the suspension for a pH of 6.0. The sample was then subjected to a study of Brookfield™ viscosity as previously described.

[0667] For the third part of the sample, the pH was reduced to 3 by a further addition of hydrochloric acid.

[0668] At the end of 20 minutes additional stirring, a measurement of conductivity of the aqueous suspension of

mineral matter was carried out using the same conductivity meter as the one used previously. This value then corresponded to the conductivity of the suspension at a pH of 3. This sample was then subjected to a study of Brookfield™ viscosity as previously described.

[0669] Test N° 66:

[0670] This test illustrates the prior art and uses, as a mineral material, a titanium dioxide sold by Tioxide under the name R-HD2 and, as a dispersing agent, a copolymer sold by Coatex under the name Coatex BR3, with a specific viscosity of 1.3.

[0671] In this test, it was impossible to continue the dispersion when the pH had dropped to 3 since the titanium oxide had caked and blocked the disperser.

[0672] The measurements of Brookfield™ viscosity and conductivity could therefore not be carried out at this pH value.

[0673] Test N° 67:

[0674] This test illustrates the invention and uses, as a mineral matter, a titanium dioxide sold by Tioxide under the name R-HD2 and, as a dispersing agent, the same copolymer as that used in Test N° 59.

[0675] All the Brookfield™ viscosity and conductivity experimental results are set out in Table 11 below.

EXAMPLE 12

[0677] The purpose of this example is to illustrate the low sensitivity to ionic strength of the aqueous suspensions according to the invention.

[0678] To do this, with the same operating method and with the same equipment as before, the mineral materials are put in suspension at a dry matter concentration of 72% in salt water with a sodium chloride content of 2 moles per litre of bipermuted water.

[0679] Test N° 68:

[0680] This test illustrates the prior art and uses, as a mineral material, a precipitated calcium carbonate sold by Solvay under the name Socal™ P3 and, as a dispersing agent, 0.73% by dry weight, with respect to the dry weight of precipitated calcium carbonate, a polyacrylic acid with a specific viscosity of 0.84.

[0681] It was impossible to put all the precipitated calcium carbonate in suspension, the spindle of the stirrer being locked before the end of the introduction of the total quantity of precipitated calcium carbonate.

[0682] Test N° 69:

[0683] This test illustrates the invention and uses, as a mineral material, a precipitated calcium carbonate (sold by

TABLE 11

				BROOKFIELD™ VISCOSITY (mPa · s)							
				INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING			
TEST N°	pH	FINAL DRY EXTRACT (%)	CONDUCTIVITY Ms/cm	10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min		
Prior art BR 3	66	3	Dispersion impossible	Dispersion impossible	Dispersion impossible	Dispersion impossible	Dispersion impossible	Dispersion impossible	Dispersion impossible	Dispersion impossible	Dispersion impossible
		6	59.5	2	24040	2592	Viscosity too high	not	measurable		
		8	59.1	1.9	214	160	302	218	165	98	
Invention	67	3	59.9	4.84	79	136	95	148	89	102	
		6	58.9	1.25	3120	374	3400	336	3240	436	
		8	59.3	0.88	760	138	860	138	660	104	

[0676] A reading of Table 11 shows that the use of a copolymer according to the invention containing, as a non-ionic monomer, at least one monomer of formula (I) results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a moderate to high mineral matter content, stable over time and having a low sensitivity to changes from the natural pH of the dispersion to acid to highly acid pHs.

Solvay under the name Socal™ P3) and, as a dispersing agent, 0.73% by dry weight, with respect to the dry weight of precipitated calcium carbonate, the same copolymer as the one used in Test N° 53.

[0684] It was possible to put all the precipitated calcium carbonate in suspension and the Brookfield™ viscosity and conductivity experimental results are set out in Table 12 below.

TABLE 12

	TEST N°	pH	CONDUCTIVITY mS/cm	BROOKFIELD™ VISCOSITY (mPa · s)					
				INITIAL		8 days BEFORE STIRRING		8 days AFTER STIRRING	
				10 rev/min	100 rev/min	10 rev/min	100 rev/min	10 rev/min	100 rev/min
Prior art	68	9	Impossible to put all the calcium carbonate in suspension						
Invention	69	9	43.8	590	446	1000	960	620	544

[0685] A reading of Table 12 shows that the use of a copolymer according to the invention containing, as a non-ionic monomer, at least one monomer of formula (I) results in the obtaining of aqueous suspensions of mineral pigments and/or fillers, according to the invention, with a moderate to high mineral matter content, stable over time and having a low sensitivity to the ionic strength of the medium, thus making it possible to obtain aqueous suspensions of mineral pigments and/or fillers which can be used in the field of drilling muds, in particular saturated salt muds and sea water muds.

EXAMPLE 13

[0686] This example relates to the use of the dispersing agent, copolymer according to the invention in the field of paint and more particularly water-based glazed paint. To do that, two tests are carried out.

[0687] Test n° 70, which illustrates the prior art, uses the dispersing agent COATEX BR 3

[0688] Test n° 71, which illustrates the invention, uses the 100% potash neutralised polymer of test n° 42.

[0689] For the test n° 70 illustrating the prior art, the constituents of the said water-based glazed paint were added in succession, these being:

[0690] 40 g of monopropylene glycol

[0691] 64 g of water

[0692] 5 g of dispersing agent COATEX BR 3 at 40% solid content

[0693] 2 g of a biocide, marketed by TROY under the name of MERGAL™ K6N

[0694] 1 g of an anti-foaming agent marketed by HENKEL under the name of NOPCO™ NDW

[0695] 150 g of a calcium carbonate marketed by OMYA under the name of OMYA DP 80 OG

[0696] 200 g of titanium dioxide marketed by MILLENNIUM under the name RHD2

[0697] These constituents are stirred during 20 minutes, and then, the other constituents are added in succession, these being:

[0698] 450 g of a styrene-acrylic binder in dispersion, marketed by RHODIA under the name of RHODOPAS™ DS 910

[0699] 30 g of butyldiglycol

[0700] 100 g of water

[0701] 4 g of a thickening agent marketed by COATEX under the name COATEX BR100P

[0702] 1 g of 28% ammonia and

[0703] 3 g of NOPCO™ NDW

[0704] After agitating the aqueous composition made up in this way for a few minutes at a pH equal to 8.7 and after observing a good slurring, the Brookfield™ viscosities of the different compositions are measured at 25° C. and at 10 revolutions per minute and 100 revolutions per minute using a standard RVT Brookfield™ viscometer fitted with the requisite spindle. They are equal to 3400 mPa.s at 10 rpm and to 1900 mPa.s at 100 rpm.

[0705] The ICI viscosity, which is a high shear (10 000 s⁻¹) viscosity, is measured with the use of a plan cone viscometer.

[0706] We obtain a ICI viscosity of 1.5.

[0707] The Stormer (KU) viscosity is also measured in Krebs Unit with the use of a Stormer viscometer.

[0708] We obtain a Stormer viscosity of 94 KU.

[0709] Test N° 71:

[0710] For this test illustrating the invention, the constituents of the water-based glazed, paint are added in succession, these being:

[0711] 40 g of monopropylene glycol

[0712] 62.7 g of water

[0713] 6.3 g of the polymer of the test n° 42 at a solid content of 31.6%

[0714] 2 g of a biocide, marketed by TROY under the name of MERGAL™ K6N

[0715] 1 g of an anti-foaming agent marketed by HENKEL under the name of NOPCO™ NDW

[0716] 150 g of a calcium carbonate marketed by OMYA under the name of OMYA DP 80 OG

[0717] 200 g of titanium dioxide marketed by MILLENNIUM under the name RHD2

[0718] These constituents are stirred during 20 minutes and then, the other constituents are added in succession, these being:

[0719] 450 g of a styrene-acrylic binder in dispersion, marketed by RHODIA under the name of RHODOPAS™ DS 910

[0720] 30 g of butyldiglycol

[0721] 100 g of water

[0722] 4 g of a thickening agent marketed by COATEX under the name COATEX BR1002

[0723] 1 g of 28% ammonia and

[0724] 3 g of NOPCO™ NDW

[0725] After agitating the aqueous composition made up in this way for a few minutes at a pH equal to 8.7 and after observing a good slurring, the Brookfield™ viscosities of the different compositions are measured at 25° C. and at 10 revolutions per minute and 100 revolutions per minute using a standard RVT Brookfield™ viscometer fitted with the requisite spindle. They are equal to 3000 mPa.s at 10 revolutions per minute and 1700 mPa.s at 100 revolutions per minute.

[0726] The ICI viscosity, which is a high shear (10 000 S⁻¹) viscosity, is measured with the use of a plan cone viscometer.

[0727] We obtain a ICI viscosity of 1.4.

[0728] The Stormer (KU) viscosity is also measured in Krebs Unit with the use of a Stormer viscometer.

[0729] We obtain a Stormer viscosity of 93 KU.

[0730] The comparison between the obtained values for the use of the copolymer according to the invention and the obtained values for the use of a polymer, usually used by the skilled man in the art, allows to note that the copolymer according to the invention can be used in the field of paints.

EXAMPLE 14:

[0731] This example concerns the use of the dispersing agent, the copolymer according to the invention, in the field of plastics materials.

[0732] For this purpose, an aqueous suspension of calcium carbonate (marble) obtained after flocculation was filtered in order to end up with a marble filtration cake with a mean diameter of 2 micrometres measured by means of a Sedi-graph™ 5100.

[0733] From this cake, the aqueous suspension of marble was prepared by introducing into the cake the required quantity by dry weight of the polymer agent of Test N° 4 according to the invention with respect to the dry weight of the said cake to be put in suspension in order to obtain an aqueous suspension of marble at a dry matter concentration of 68%.

[0734] Once this suspension had been produced, it was dried at a temperature of less than 105° C. by the use of a laboratory dryer of the Niro™ type.

[0735] The powder obtained without any agglomerate was then divided into two samples, one of which was to be the

subject of the dispersion test in a thermoplastic resin and the other the subject of the dispersion test in a thermosetting resin.

[0736] Test N° 72:

[0737] This test, illustrating the invention, represents the test on the dispersion of the marble powder, previously obtained, in a thermoplastic resin.

[0738] For this purpose, 300 grams of previously prepared marble in powder form with a mean diameter of 2 µm was introduced into a Z-arm Guittard mixer with a capacity of 1.5 litres and having a vessel electrically heated to 240° C.

[0739] After 15 minutes of preliminary heating of the load at 240° C., 3 grams of commercial available zinc stearate and 125.5 grams of polypropylene homopolymer sold by the company Appryl under the name PPH 3120MN1 were introduced.

[0740] The whole was mixed for 20 minutes at this temperature and at a speed of 42 revolutions/minute.

[0741] With the mixture thus prepared, a calendering of part of this mixture was then carried out in the form of sheets which were cut into small cubes 2 to 3 millimetres square and whose MFI fluidity index was measured at 230° C. under a load of 2.16 kg and 10 kg with a 2.09 mm diameter die.

[0742] The MFI obtained was 8.0 g/10 min (230° C.-2.16 kg-2.09 mm) and 132 g/10 min (230° C.-10 kg-2.09 mm).

[0743] This MFI result shows that the use of the agent, the copolymer according to the invention, results in loaded thermoplastic compositions which can be used in the field of thermoplastics.

[0744] Test N° 73:

[0745] This test, illustrating the invention, represents the test for the dispersion of marble powder, previously obtained, in a thermosetting resin of the unsaturated polyester type.

[0746] For this purpose, in a 500 ml metallic box, 90 grams of unsaturated polyester resin reference Palapreg P18 from BASF, 60 grams of an additive called "Low Profile" and available under the reference LP40A from Union Carbide and 300 grams of the marble powder obtained were weighed.

[0747] After 24 hours of storing at rest, a presence of settling or sedimentation before homogenisation was noted.

[0748] Homogenisation of the mixture by stirring with a spatula was then carried out, and then the Brookfield™ viscosity at 100 revolutions/min was measured after this 24 hours by means of a Brookfield™ type RVT viscometer equipped with the module 7.

[0749] It was 32,000 mPa.s.

[0750] It should be noted that this premixing of the polyester and calcium carbonate can be used for manufacturing preimpregnates of the SMC (Sheet Moulding Compound) or BMC (Bulk Moulding Compound) type.

EXAMPLE 15

[0751] This example concerns the use of an aqueous suspension of mineral fillers according to the invention in

the field of paper. It relates more specifically to the determination of the different Brookfield™ viscosity and water retention values of the different 100% calcium carbonate coating colors.

[0752] Test N° 74:

[0753] This test illustrates the prior art and uses a coating color composed of:

[0754] 100 parts, expressed as dry matter, of an aqueous suspension according to the prior art, at 72% by dry weight of calcium carbonate having a particle such as 75% of the particles have a diameter less than 1 μm determined by Sedigraph™ 5100 and having 0-75% by dry weight of a dispersing agent marketed by Coatex under the name M 777,

[0755] 12 parts, expressed as dry matter, of a styrene-butadiene latex sold by Dow under the name "DL 950",

[0756] 0.5 parts, expressed as dry matter, of a water retention agent marketed by Coatex under the name Rheocoat™ 35.

[0757] The solid content of the coating color is about 65%.

[0758] Test N° 75:

[0759] This test illustrates the invention and uses a coating color composed of:

[0760] 100 parts, expressed as dry matter, of an aqueous suspension according to the invention, at 72% by dry weight of calcium carbonate having a particle such as 75% of the particles have a diameter less than 1 μm determined by Sedigraph™ 5100 and having 0-75% by dry weight of a dispersing agent according to the invention and composed of 20% by weight of acrylic acid; 80% of methoxy PEG 2000 methacrylate having a specific viscosity of 1.26,

[0761] 12 parts, expressed as dry matter, of a styrene-butadiene latex sold by Dow under the name "DL 950",

[0762] 0.5 parts, expressed as dry matter, of a water retention agent marketed by Coatex under the name Rheocoat™ 35.

[0763] The solid content of the coating color is about 65%.

[0764] The results of the measurements of Brookfield™ viscosity determined at 10 and 100 revolutions per minute at 25° C. by means of a Brookfield™ viscometer type DV-1 equipped with the appropriate spindle are:

[0765] For test n° 74 according to the prior art:

[0766] Brookfield™ viscosity at 10 rpm=8000 mPa.s

[0767] Brookfield™ viscosity at 100 rpm=1500 mPa.s

[0768] For test n° 75 according to the invention.

[0769] Brookfield™ viscosity at 10 rpm=9200 mPa.s

[0770] Brookfield™ viscosity at 100 rpm=1800 mPa.s

[0771] The results of the water retention measurements obtained according to the following method is:

[0772] For test n° 74 according to the prior art, the water volume after 10 minutes is 3.2 ml,

[0773] For test n° 75 according to the invention, the water volume after 10 minutes is 2.8 ml.

[0774] So, in order to measure the water retentions, the paper coating color to be tested is subjected to a pressure of 100 psi (7 bars) in a standard cylinder, equipped with a surface of the filter paper type capable of allowing water to pass.

[0775] After 10 minutes, the volume of water collected is measured in ml.

[0776] The lower the volume of water collected at the end of 10 minutes, the better is the retention.

[0777] To do this, use is made of an "API Fluid Loss Measurement" filter press from Baroid, which is composed essentially of a clamp provided with a clamping screw for locking the three parts of the filter body.

[0778] This body is composed of:

[0779] a base with a hole provided with a nozzle through which the filtrate flows. This base supports a metallic sieve with a mesh of 60 to 80, on which is placed the 90 mm diameter filter paper (Whatman™ N°50), the equivalent of which is the DURIEUX BLEU™ N° 3 type,

[0780] a cylinder with an inside diameter of 76.2 mm and a height of 128 mm,

[0781] a cover provided with a compressed gas inlet, whose seal with the cylinder is provided by means of a flat joint, of the same type as those placed on the base.

[0782] To use the filter press, the following are fitted in the following order:

[0783] the joint on the base

[0784] the sieve on the joints

[0785] the filter paper on the sieve

[0786] the second joint on the filter paper

[0787] and the cylinder is fitted on the base before locking the bayonet system.

[0788] Then it is filled with the coating color to be tested (approximately 480 g up to 3 cm from the top of the cylinder) before placing the cover on the cylinder, interposing a joint.

[0789] Then the assembly is placed in the clamp and is locked by means of the clamping screw, and then a graduated tube is arranged underneath the nozzle.

[0790] A pressure of 7 bars is applied, simultaneously triggering a chronometer.

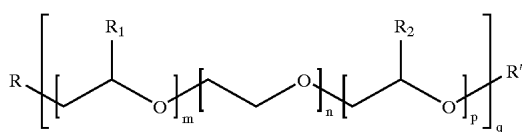
[0791] After 20 minutes the volume of fluid collected in the test tube is noted. The accuracy of the result obtained is ± 0.2 ml.

[0792] The reading of the previous results shows that the characteristics of the rheology and of the water-retention

concerning the test according to the invention allow to use the aqueous suspensions according to the invention in the field of paper and more particularly in the coating of paper.

1. The use of a slightly anionic and water-soluble copolymer as a dispersing agent and/or an aid to the grinding of mineral pigments and/or fillers in aqueous suspension, characterised in that the said copolymer consists of:

- a) at least one anionic monomer with an unsaturated ethylenic chain and a monocarboxylic function chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid or diacid hemiesters such as the C₁ to C₄ monoesters of maleic or itaconic acids, or mixtures thereof,
- b) possibly at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof chosen from amongst monomers with an unsaturated ethylenic chain and a dicarboxylic function such as crotonic, isocrotonic, cinnamic, itaconic, maleic or citraconic acid or carboxylic acid anhydrides, such as maleic anhydride, or chosen from amongst monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methylpropane sulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as vinyl phosphoric acid, ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphonic function such as phosphonic vinyl acid, or mixtures thereof
- c) at least one non-ionic monomer with an unsaturated ethylenic chain of formula (I):



in which

m and p represent a number of alkylene oxide units less than or equal to 150,

n represents a number of ethylene oxide units less than or equal to 150,

q represents a number at least equal to 1 and such that

$$5 \leq (m+n+p)q \leq 150$$

R₁ is hydrogen or the methyl or ethyl radical

R₂ is hydrogen or the methyl or ethyl radical

R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as acrylurethane, methacrylure-

thane, α-α' dimethylisopropenyl benzylurethane or allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

R' represents a hydrocarbon radical having 1 to 5 carbon atoms

d) possibly a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, aliphatic styrene and derivatives thereof, and

e) possibly at least one monomer having at least two unsaturated ethylenic chains and chosen from the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, allyl maleates, methylenebisacrylamide, methylenebismethacrylamide, tetraallyloxyethane, the triallylcyanurates, and the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose or others,

the total of constituents a), b), c), d) and e) being equal to 100%

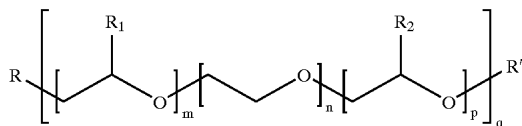
and in that the said copolymer has a specific viscosity of no more than 10, preferably no more than 5 and highly preferentially no more than 2.

2. The use of a slightly anionic and water-soluble copolymer according to claim 1, characterised in that the said copolymer consists, expressed by weight, of:

a) 2% to 85% and even more particularly 2% to 80% of at least one anionic monomer with an unsaturated ethylenic chain and a monocarboxylic function chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid or the hemiesters of diacids such as the C₁ to C₄ monoesters of maleic or itaconic acids, or mixtures thereof,

b) from 0% to 80% and even more particularly from 0% to 50% and very particularly from 0% to 20% of at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof chosen from amongst monomers with an unsaturated ethylenic chain and a dicarboxylic function such as crotonic, isocrotonic, cinnamic, itaconic, maleic or citraconic acid or carboxylic acid anhydrides, such as maleic anhydride, or chosen from amongst monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methylpropane sulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as vinyl phosphoric acid, ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphonic function such as phosphonic vinyl acid, or mixtures thereof

- c) from 20% to 95% of at least one monomer with an unsaturated ethylenic chain of formula (I):



in which

m and p represent a number of alkylene oxide units less than or equal to 150,

n represents a number of ethylene oxide units less than or equal to 150,

q represents a number at least equal to 1 and such that

$$5 \leq (m+n+p)q \leq 150$$

R₁ is hydrogen or the methyl or ethyl radical

R₂ is hydrogen or the methyl or ethyl radical

R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as acrylurethane, methacrylurethane, α - α' dimethylisopropenyl benzylurethane or allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

R' represents a hydrocarbon radical having 1 to 5 carbon atoms

- d) from 0% to 50% of a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, alphasubstituted styrene and derivatives thereof, and

- e) from 0% to 3% of at least one cross-linking monomer chosen from the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, allyl maleates, methylenebisacrylamide, methylenebismethacrylamide, tetrallyloxyethane, the triallylcyanurates, or the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose or others,

the total of constituents a), b), c), d) and e) being equal to 100%

and in that the said copolymer has a specific viscosity of no more than 10, preferably no more than 5 and highly preferentially no more than 2.

3. The use of a slightly anionic and water-soluble copolymer according to claim 2, characterised in that:

- a) the anionic monomer with unsaturated ethylenic chains and a monocarboxylic function is preferably chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid,

- b) the anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or

phosphonic function or a mixture thereof is preferably chosen from amongst the monomers with an unsaturated ethylenic chain and a dicarboxylic function such as itaconic or maleic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methyl-propanesulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or mixtures thereof

- c) the non-ionic monomer with an unsaturated ethylenic chain of formula (I) is such that

R₁ represents hydrogen or the methyl or ethyl radical

R₂ represents hydrogen or the methyl or ethyl radical

R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters as well as unsaturated urethanes such as acrylurethane, methacrylurethane, α - α' dimethylisopropenyl benzylurethane, allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

R' represents a hydrocarbon radical having 1 to 5 carbon atoms

- d) the monomer of the acrylamide or methacrylamide type or derivatives thereof is chosen from amongst acrylamide or methacrylamide, and the non water-soluble monomer is chosen from amongst ethyl acrylate or styrene

- e) the cross-linking agent is chosen from amongst the group consisting of OL ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, the allyl maleates, methylenebisacrylamide, methylenebismethacrylamide, tetrallyloxyethane, the triallylcyanurates, the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose or others.

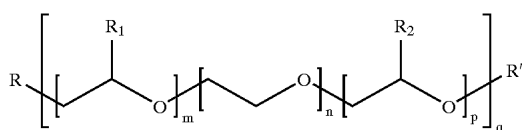
4. The use of a slightly anionic and water-soluble copolymer according to any one of claims 1 to 3, characterised in that the said copolymer obtained in acid form and possibly distilled can also be partially or completely neutralised by one or more neutralisation agents having a monovalent neutralising function or having a polyvalent neutralising function such as for the monovalent function, those chosen from the group consisting of alkali cations, in particular sodium, potassium, lithium, ammonium or the aliphatic and/or cyclic primary, secondary or tertiary amines such as stearylamine, the ethanolamines (mono-, di-, triethanolamine), mono and diethylamine, cyclohexylamine, methylcyclohexylamine or, for the polyvalent function, those chosen from the group consisting of alkaline-earth divalent cations, in particular magnesium and calcium, or zinc, also consisting of trivalent cations, in particular aluminium, or certain cations with a higher valency.

5. The use of a slightly anionic and water-soluble copolymer according to claim 4, characterised in that the said copolymer resulting from the copolymerisation reaction can, possibly before or after the complete or partial neutralisation

reaction, be treated and separated into several phases, according to static or dynamic methods known to skilled man in the art, by means of one or more polar solvents belonging to the group consisting of water, methanol, ethanol, propanol, isopropanol, the butanols, acetone, tetrahydrofuran or mixtures thereof.

6. A dispersing agent and/or an agent for assisting the grinding of mineral pigments and/or fillers in aqueous suspension, characterized in that the said agent is a copolymer consisting of:

- a) at least one anionic monomer with an unsaturated ethylenic chain and a monocarboxylic function chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid or diacid hemiesters such as the C₁ to C₄ monoesters of maleic or itaconic acids, or mixtures thereof,
- b) possibly at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof chosen from amongst monomers with an unsaturated ethylenic chain and a dicarboxylic function such as crotonic, isocrotonic, cinnamic, itaconic, maleic or citraconic acid or carboxylic acid anhydrides, such as maleic anhydride, or chosen from amongst monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methylpropane sulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as vinyl phosphoric acid, ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphonic function such as phosphonic vinyl acid, or mixtures thereof
- c) at least one non-ionic monomer with an unsaturated ethylenic chain of formula (I):



in which

m and p represent a number of alkylene oxide units less than or equal to 150,

n represents a number of ethylene oxide units less than or equal to 150,

q represents a number at least equal to 1 and such that $5 \leq (m+n+p)q \leq 150$

R₁ is hydrogen or the methyl or ethyl radical

R₂ is hydrogen or the methyl or ethyl radical

R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic,

itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as acrylurethane, methacrylurethane, dimethylisopropenyl benzylurethane, allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

R' represents a hydrocarbon radical having 1 to 5 carbon atoms

d) possibly a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, aliphatic styrene and derivatives thereof, and

e) possibly at least one cross-linking monomer chosen from the group consisting of ethylene glycol dimethacrylate, trimethylolpropane-triacrylate, allyl acrylate, allyl maleates, methylene-bisacrylamide, methylenebismethacrylamide, tetraallyl-oxethane, the triallylcyanurates, the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose and others,

the total of constituents a), b), c), d) and e) being equal to 100%

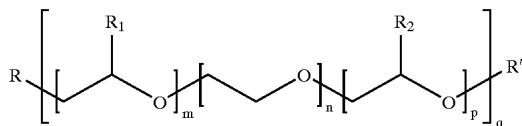
and in that the said copolymer has a specific viscosity of no more than 10, preferably no more than 5 and highly preferentially no more than 2.

7. A dispersing agent and/or an agent for assisting the grinding of mineral pigments and/or fillers in aqueous suspension according to claim 6, characterised in that the said agent is a copolymer consisting, expressed by weight, of:

a) 2% to 85% and even more particularly 2% to 80% of at least one anionic monomer with an unsaturated ethylenic chain and a monocarboxylic function chosen from amongst the monomers with an unsaturated ethylenic chain and a monocarboxylic function such as acrylic or methacrylic acid or the hemiesters of diacids such as the C₁ to C₄ monoesters of maleic or itaconic acids, or mixtures thereof,

b) from 0% to 80% and even more particularly from 0% to 50% and very particularly from 0% to 20% of at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof chosen from amongst monomers with an unsaturated ethylenic chain and a dicarboxylic function such as crotonic, isocrotonic, cinnamic, itaconic, maleic or citraconic acid or carboxylic acid anhydrides, such as maleic anhydride, or chosen from amongst monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methylpropane sulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as vinyl phosphoric acid, ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphonic function such as phosphonic vinyl acid, or mixtures thereof

- c) from 20% to 95% of at least one monomer with a non-ionic unsaturated ethylenic chain of formula (I):



in which

m and p represent a number of alkylene oxide units less than or equal to 150,

n represents a number of ethylene oxide units less than or equal to 150,

q represents a number at least equal to 1 and such that $5 \leq (m+n+p)q \leq 150$

R₁ is hydrogen or the methyl or ethyl radical

R₂ is hydrogen or the methyl or ethyl radical

R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters and unsaturated urethanes such as acrylurethane, methacrylurethane, dimethylisopropenyl benzylurethane or allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

R' represents a hydrocarbon radical having 1 to 5 carbon atoms

- d) from 0% to 50% of a monomer of the acrylamide or methacrylamide type or derivatives thereof and mixtures thereof or one or more non water-soluble monomers such as alkyl acrylates or methacrylates, vinyl compounds such as vinyl acetate, vinylpyrrolidone, styrene, aliphathylstyrene and derivatives thereof, and

- e) from 0% to 3% of at least one cross-linking monomer chosen from the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, allyl maleates, methylenebisacrylamide, methylenebis-methacrylamide, tetraallyloxyethane, the triallyl-cyanurates, the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose and others,

the total of constituents a), b), c), d) and e) being equal to 100%

and in that the said copolymer has a specific viscosity of no more than 10, preferably no more than 5 and highly preferentially no more than 2.

8. A dispersing agent and/or agent assisting the grinding of mineral pigments and/or fillers in aqueous suspension according to claim 7, characterised in that the said agent is a copolymer consisting of:

- a) at least one anionic monomer with an unsaturated ethylenic chain and a monocarboxylic function is preferably chosen from amongst the monomers with an unsaturated ethylenic chain and monocarboxylic functions such as acrylic or methacrylic acid,

- b) possibly at least one anionic monomer with an unsaturated ethylenic chain and a dicarboxylic or sulphonic or phosphoric or phosphonic function or a mixture thereof is preferably chosen from amongst the monomers with an unsaturated ethylenic chain and a dicarboxylic function such as itaconic or maleic acid or preferentially chosen from amongst the monomers with an unsaturated ethylenic chain and a sulphonic function such as acrylamido-methyl-propanesulphonic acid, sodium methallylsulphonate, vinyl sulphonic acid and styrene sulphonic acid or preferentially chosen from amongst the monomers with an unsaturated ethylenic chain and a phosphoric function such as ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and ethoxylates thereof or mixtures thereof

- c) at least one non-ionic monomer with an unsaturated ethylenic chain of formula (I) such that

R₁ represents hydrogen or the methyl or ethyl radical

R₂ represents hydrogen or the methyl or ethyl radical

R represents the polymerisable unsaturated radical, belonging to the group of acrylic, methacrylic, maleic, itaconic, crotonic or vinylphthalic esters as well as unsaturated urethanes such as acrylurethane, methacrylurethane, α - α' dimethylisopropenyl benzylurethane or allylurethane, and to the group of allyl or vinyl ethers or to the group of ethylenically unsaturated amides,

R' represents a hydrocarbon radical having 1 to 5 carbon atoms

- d) possibly one monomer of the acrylamide or methacrylamide type or derivatives thereof preferentially chosen from amongst acrylamide or methacrylamide, and at least one non water-soluble monomer preferentially chosen from amongst ethyl acrylate or styrene

- e) possibly at least one cross-linking agent chosen from amongst the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, the allyl maleates, methylenebisacrylamide, methylenebismethacrylamide, tetraallyloxyethane, the triallylcyanurates, the allyl ethers obtained from polyols such as pentaerythritol, sorbitol, sucrose or others.

9. A dispersing agent and/or an agent assisting the grinding of mineral pigments and/or fillers in aqueous suspension according to any one of claims 6 to 8, characterised in that the said agent is a copolymer neutralised with one or more neutralisation agents having a monovalent neutralising function or having a polyvalent neutralising function such as for the monovalent function, those chosen from the chosen from the group consisting of alkaline cations, in particular sodium, potassium, lithium, ammonium or the aliphatic and/or cyclic primary, secondary or tertiary amines such as stearylamine, the ethanolamines (mono-, di-, triethanolamine), mono and diethylamine, cyclohexylamine, methylcyclohexylamine or, for the polyvalent function, those chosen from the group consisting of alkaline-earth divalent cations, in particular magnesium and calcium, or zinc, also consisting of trivalent cations, in particular aluminium, or certain cations with a higher valency.

10. A dispersing agent and/or agent for assisting the grinding of mineral pigments and/or fillers in aqueous suspension according to claim 9, characterised in that the said copolymer resulting from the copolymerisation reaction can, possibly before or after the complete or partial neutralisation reaction, be treated and separated into several phases, according to static or dynamic methods known to the skilled man in the art, by means of one or more polar solvents belonging to the group consisting of water, methanol, ethanol, propanol, isopropanol, the butanols, acetone, tetrahydrofuran or mixtures thereof.

11. An aqueous suspension of fillers and/or pigments characterised in that it contains the agent according to one of claims 6 to 10 and more particularly in that it contains from 0.05% to 5% by dry weight of the said agent with respect to the total dry weight of the fillers and/or pigments, and even more particularly 0.3% to 1.0% by dry weight of the said agent with respect to the total dry weight of the fillers and/or pigments.

12. An aqueous suspension of fillers and/or pigments according to claim 11, characterised in that the filler and/or pigment is chosen from amongst natural calcium carbonate such as calcite, chalk or marble, synthetic calcium carbonate, also referred to as precipitated calcium carbonate, dolomites, magnesium hydroxide, kaolin, talc, gypsum, titanium dioxide or aluminium hydroxide or any other filler and/or pigment normally used in the papermaking or petroleum field.

13. An aqueous suspension of fillers and/or pigments according to claim 12, characterised in that it is only slightly

sensitive to the pH and ionic strength of the media and in that it has a low Zeta potential, that is to say a Zeta potential of between 0 and -30 mV and preferentially between 0 and -20 mV.

14. The use of the aqueous suspension of fillers and/or pigments according to any one of claims 11 to 13 in the papermaking field and more particularly in the manufacture and/or coating of sheets of paper.

15. Sheets of paper containing the aqueous suspension of fillers and/or pigments according to any one of claims 11 to 13.

16. The use of the aqueous suspension of fillers and/or pigments according to any one of claims 11 to 13 in the field of drilling muds used for petroleum prospecting or extraction, in particular in the field of saturated salt muds and sea water muds.

17. A drilling mud containing the aqueous suspension of fillers and/or pigments according to any one of claims 11 to 13.

18. The use of the dispersing agent and/or of the agent for assisting the grinding of mineral pigments and/or fillers in aqueous suspension according to any one of claims 6 to 10 in the field of paints.

19. The use of the dispersing agent and/or of the agent for assisting the grinding of mineral pigments and/or fillers in aqueous suspension according to any one of claims 6 to 10 in the field of plastic materials and more particularly in the field of thermoplastic or thermosetting resins.

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(54) Title: IMPROVED COATED INK JET PAPER

(57) Abstract: An improved coated sheet product especially useful in conjunction with inkjet printers comprises a substrate carrying a coating on at least one surface, characterised in that the coating includes (i) a pigment comprising calcium carbonate; (ii) a binder for component (i) comprising a major proportion of a polymer carrying -O-, -CO-, -OCO- and/or -COO- groups in its side-chains; and (iii) at least at the surface of said coating, a water-soluble salt of a Group II, Group III or transition metal.



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Improved Coated Ink Jet Paper

- 5 The present invention relates to an improved coated paper especially useful in conjunction with inkjet printers.

Inkjet printers are widely used both for the domestic market and, increasingly, for the commercial market. Currently, one major drawback of using inkjet printers is the provision
10 of suitable papers, particularly those capable of carrying photo-quality prints having a gloss or semi-gloss finish. Current photo-quality papers, although technically satisfactory, are coated papers which achieve their good results by the use of extremely expensive coating materials or processes, making them unsuitable for bulk use. Typically, the coatings
15 present on such papers are based on swellable polymer coatings, micropigments based on silicates or aluminates, or coatings which receive a gloss finish as a result of a cast coating process. Silica is widely used as a pigment. All of these approaches provide good technical results, but are very expensive.

The results obtained when using papers designed for use in offset printers in inkjet printers
20 are unsatisfactory. Such papers generally contain a coating comprising a pigment such as calcium carbonate together with a binder such as a styrene/butadiene latex.

GB 2,301,845 describes a recording sheet, especially a tracing sheet or an uncoated cellulose-based paper, for use in inkjet printers, wherein at least a usable surface includes a
25 combination of a water soluble cationic substance, for example a soluble polyvalent metal salt (for example magnesium sulfate) or a cationic polymer, and a water soluble binder. Suitable binders are polyvinyl pyrrolidone, polyvinyl alcohol, starches, and gelatine.

WO 00/44568 describes a recording sheet for use on a digital press which includes either an
30 insoluble mineral filler including a Lewis acid, for example insoluble aluminium trihydrate, in the base paper, or a soluble or insoluble metal from Groups II and III or the Transition metals, for example magnesium sulfate, at the surface.

EP 1775141 describes a similar recording sheet, in which a composition comprising a divalent metal salt and a starch is applied to the surface of a substrate comprising ligno cellulosic fibres.

- 5 JP 2005-066925 discloses a specific pigment which has very small nanoparticles, and which is prepared by complexing zinc into a calcium carbonate pigment (i.e. there is no free salt present in the final coating containing the pigment). The resulting pigment is used in the presence of a polymer system containing a minor proportion of hydrophilic polymers, together with an allylic polymer and cationic (polyamine) polymer.

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WO 2003/104336 describes a coating composition comprising a blend of at least two dye fixatives, at least one of which is a cationic polymer, and at least one of which is a polyvalent metal salt. JP 2007-160746 describes an inkjet recording sheet consisting of an ink receptive layer comprising a water-insoluble resin and a water-soluble resin together

- 15 with an inorganic pigment and a water-soluble magnesium salt. WO 2006/049545 describes a pigment composition in the form of an aqueous dispersion or slurry comprising porous aggregates and extender particles. WO 2006/116878 discloses a coating composition comprising a styrene acrylate copolymer; and organic cationic polyelectrolyte; at least one inorganic pigment; a binder; and wetting agent; and a lithium, sodium or
20 potassium salt. US 2006/0172093 discloses an inkjet recording material having a pigment layer and an ink recording layer, both of defined composition. None of these documents discloses the use of a specific combination of ingredients having the particular characteristics of the present invention.

- 25 There remains a need for a photo-quality paper or paper-like product which can be used with good effect in inkjet printers and which can be manufactured at reasonable cost.

We have now found that the use of a very specific combination of ingredients in a coating provides an economical paper capable of carrying photo-quality prints delivered by an

- 30 inkjet printer.

Accordingly, the present invention provides a sheet product comprising a substrate carrying a coating on at least one surface, characterised in that the coating includes (i) a pigment comprising calcium carbonate; (ii) a binder for component (i) comprising a major

proportion of a polymer carrying -O-, -CO-, -OCO- and/or -COO- groups in its side-chains; and (iii) at least at the surface of said coating, a water-soluble salt of a Group II, Group III or transition metal.

- 5 Although other pigments in addition to calcium carbonate may be present in component (i) if desired, preferably no aluminate or silicate is present. In one embodiment of the invention, the pigment comprises a major proportion (i.e. at least 50% by weight), preferably at least 80% by weight, of calcium carbonate. For example, calcium carbonate may be the only pigment present. In another embodiment of the invention, one or more
10 additional pigments may be present. In this embodiment, a calcined clay may be present, for example in an amount of from 10 to 40, preferably from 20 to 30% by weight, based on the combined weight of calcium carbonate and clay.

- The calcium carbonate may be in the form of precipitated calcium carbonate or ground
15 calcium carbonate, the latter being preferred. In general, component (i) will be derived from a dispersion, for example a dispersion of calcium carbonate containing appropriate dispersion stabilizers. Preferably the pigment has a mean particle size of 15 microns or less, for example 10 microns or less. In general, the smaller the particle size of the pigment, the higher the gloss obtainable on the sheet product. For a very high gloss finish,
20 particles having a mean particle size of 5 microns or less, especially 2 microns or less, are preferred.

- Preferably the coating on the sheet product according to the invention is free from pigments in microparticulate form, especially silicates and aluminates. Microparticulate pigments
25 (often known as nanoparticulate pigments) are generally synthetic pigments prepared by precipitation from a solution. The primary mean particle size is generally less than about 50nanometers, especially less than 30nanometers, and typically 10-20 nanometers. The particles may, however, form agglomerates where the agglomerates have particle sizes of up to about 200-300nanometers (i.e. 0.2-0.3microns). The pigment used in the present
30 invention preferably has a mean particle size of greater than 0.2microns, preferably greater than 0.3microns.

The binder used in the present invention comprises a major proportion (i.e. at least 50% by weight), and preferably at least 80% by weight, of the specified binders, which are

hydrophilic binders. Suitable binders for use in component (ii) include polyvinyl acetate, vinyl acetate copolymers, polyvinyl alcohol, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, sodium alginate or starch, or mixtures thereof.

Preferably the binder is used in the form of a latex, i.e. in the form of a stabilised emulsion
5 comprising either liquid droplets or solid particles dispersed in a continuous phase. Vinyl polymers are preferred, with the use of polyvinyl acetate, especially self crosslinking vinyl acetate homopolymer, being preferred. Two or more different binders of the type specified may be present, for example the binder may comprise a major proportion of polyvinyl acetate together with a minor proportion of another of the specified binders, for example
10 polyvinyl alcohol (which has the effect of enhancing the efficiency of optical brighteners) or a cellulose derivative such as hydroxyethyl cellulose or sodium carboxymethyl cellulose (which is effective as a rheology modifier and a water retention aid). Alternatively, polyvinyl acetate may be the only binder present in component (ii).

15 The specified polymers are generally anionic in nature, and therefore the coatings used in the present invention preferably contain only a low proportion, or no, cationic polymer. Preferably the weight ratio in the coating of cationic polymer to the polymer carrying -O-, -CO-, -OCO- and/or -COO- groups in its side-chains is less than 1:1, especially less than 1:2, most preferably less than 1:5.

20 The ratio of component (i) to component (ii) may vary within conventional limits, for example with component (i) comprising at least 55% by weight, for example from 65 to 95%, especially from 75 to 95%, by weight based on the combined weight of components (i) and (ii).

25 Component (iii) may be any water-soluble salt of a metal from Group II or Group III or a transition metal. Salts of Group II or Group III metals or first row transition metals, for example calcium, magnesium, aluminium, manganese or zinc, especially calcium, magnesium or manganese, are preferred. The salt may for example be a halide, sulfate or
30 nitrate, for example calcium, magnesium or manganese sulfate or nitrate. The use of calcium chloride, manganese sulfate or, especially, magnesium sulfate, is preferred.

Preferably the quantity of water-soluble salt present is in the range of from 2 to 35, preferably 5 to 25, more preferably 10 to 20, parts by weight per hundred parts dry weight of calcium carbonate.

- 5 Thus, a preferred sheet product according to the present invention comprises (i) a pigment comprising at least 80% by weight of calcium carbonate; (ii) a binder for component (i) comprising at least 80% by weight of vinyl acetate; and (iii) at least at the surface of said coating, a water-soluble salt of a Group II, Group III or transition metal salt, especially magnesium sulfate, preferably in an amount of from 5 to 25 parts by weight per hundred
10 parts dry weight of calcium carbonate.

- The coating of the sheet product according to the invention may consist of a single layer, or it may contain two or more separate layers. The binder of component (ii), e.g. polyvinyl acetate, acts as a binder for the pigment of component (i), and must therefore be present in
15 the same layer as the pigment. Component (iii) may be present in the same layer, or a different layer, provided that it is present at the surface of the overall coating. In the simplest embodiment of the invention, all three of components (i), (ii) and (iii) are present in a single layer. In a further embodiment, two (or more) layers may be present, with component (iii) being present in at least the layer furthest away from the surface of the
20 substrate. The use of a single layer including components (i) and (ii) (and optionally component (iii)) is possible, or two (or more) such layers may be present. A higher gloss appearance is obtained if a first layer containing at least components (i) and (ii) adjacent the surface of the substrate is covered with a second layer containing components (i) and (ii), the mean particle size of the pigment in said second layer being smaller than the mean
25 particle size of the pigment in said first layer. The gloss of the sheet can also be readily manipulated by processing after application of the coating, for example by calendering.

- A solution of component (iii) may if desired be applied on top of one or more layers comprising components (i) and (ii) to produce the finished coating. This solution may be a
30 simple aqueous solution of component (iii), or it may contain other additives, for example one or more viscosifiers. Many substances conventionally used as binders may also be used as viscosifiers. Thus the solution of component (iii) may if desired contain additional binder (acting as a viscosifier) in addition to the binder already present in association with

the pigment. If additional binder is present, this may be the same binder as that of component (ii), or a different binder.

5 The coating or any layer comprised in the coating may comprise any other desired additive which does not interfere with the performance of the finished paper. The coating may for example contain optical brighteners, colourants, dispersants, surfactants, defoaming agents, preservatives, water retention aids and pH control agents. Some of these ingredients may have multiple functions, for example, certain water retention aids may also function as binders. Starch may be present, but preferably said coating is free from starch.

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The substrate of the sheet product of the invention is preferably paper, although plastic sheet materials which simulate the properties of paper (so-called "synthetic paper") can alternatively be used. The substrate may be of any desired weight or quality suitable for use in inkjet printers. The weight or quality is generally determined by the intended application. For example, business forms and transactional documents may have a low substrate weight such as 45 to 60g/m², giving after coating a finished weight of around 60 to 100g/m². Papers aimed at promotional print may have finished weights around, say, 135g/m², and those aimed at publishing grades will be higher, say, around 160g/m². Board weights may be used for applications such as covers, menus, greetings cards, and packaging, and in this case the substrate could be in the range of 250 to 300g/m² or higher. Different types of inkjet printers are used for different substrate weight ranges. The finished sheet according to the invention may if desired be incorporated into a composite, for example to form a label, or laminated, for example to produce a heavyweight board, for example for packaging.

25

The coating or any layer comprised in the coating may be applied to the substrate by any conventional method, for example by size press treatment, dip coating, roll coating, extrusion coating, airknife coating, curtain coating or, especially, blade coating. If present, a separate aqueous solution of component (iii) may additionally be applied as a wash or a spray.

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The invention also provides a method of printing an image, which comprises applying water-based ink to a sheet product according to the present invention, using an inkjet printer and a water-based ink. Any water-based inkjet ink may be used in association with

the sheet product of the present invention, for example a dye-based ink or a pigment-based ink, with the use of pigment-based inks generally being preferred.

The invention further provides the use of a combination of

- 5 (i) a pigment comprising calcium carbonate; (ii) a binder for component (i) comprising a major proportion of a polymer carrying -O-, -CO-, -OCO- and/or -COO- groups in its side-chains; and (iii) a water-soluble salt of a Group II, Group III or transition metal salt; in a coating for a sheet product, in order to render said sheet product suitable for use in an inkjet printer using a water-based ink.

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The following Examples illustrate the invention.

Example 1

A paper sheet coated with a pre-coat layer of the composition shown in Table I was

- 15 prepared as follows.

Table I

MATERIAL	PARTS DRY	%Wt/Wt DRY	DRY Wt / Kg	SOLIDS	Net wt./Kg	
WATER					1.60	
Mowiol 4-98	0.90	0.81	0.57	25.00%	2.27	Binder
Caustic soda	0.08	0.07	0.05	25.00%	0.20	pH adjuster
Carbital 60	100.00	90.20	63.14	77.00%	82.00	Pigment
Emultex 738	9.50	8.57	6.00	45.00%	13.33	Binder
Viscolam 30	0.08	0.07	0.05	29.00%	0.17	Rheology modifier
Optiblanc KLN	0.27	0.24	0.17	47.50%	0.35	Optical Brightener
Nopcomaster	0.03	0.03	0.02	35.00%	0.06	Antifoam
TOTALS	110.86	100.00	70.00	70.0%	100.00	

- 20 Polyvinyl alcohol (Mowiol 4-98 (Trade Mark) manufactured by Kuraray Co., Ltd) was prepared in water at 25% solids at 90°C. The mixture was allowed to cool and a portion of 0.07 parts by weight of caustic soda was added to 0.8 parts by weight of the polyvinyl alcohol. A portion of 90.2 parts by weight of ground calcium carbonate (Carbital 60 (Trade Mark) supplied by Imerys as slurry of 77% solids and having a 60% content of particles
- 25 less than 2 microns and a mean particle size (diameter) of 1.83 microns) was added to the liquid mixture and allowed to stir for 10 minutes.

A portion of 9 parts by weight of a water based dispersion (a latex) of self cross-linking vinyl acetate homopolymer (Emultex 378 (Trade Mark) supplied by Synthomer Ltd) was

added. The mix was stirred for 10 minutes and 0.07 parts by weight of a polyacrylic thickener (Viscolam 30 (Trade Mark) supplied by Lamberti SpA) was added followed by 0.24 parts by weight of optical brightener (Optiblanc KLN (Trade Mark)) and 0.03 parts of antifoam (Nopcomaster (Trade Mark)). The mix was allowed to stir for 30 minutes. The aqueous mix was coated in a dry solids amount of 20g/m² on one side of the paper sheet using conventional blade coating.

The resulting sheet was provided with a further, glossy, ink receptive layer, of the composition shown in Table II.

Table II

MATERIAL	PARTS DRY	%W/W DRY	DRY W / Kg	SOLIDS	WET Wt / Kg	
WATER					2.34	
Magnesium Sulfate	15.00	12.22	4.89	10.00%	48.87	Divalent salt
Mowiol 4-98	0.46	0.37	0.15	25.00%	0.60	Binder
Setacarb 80	100.00	81.46	32.58	76.00%	42.87	Pigment
Ca stearate	0.25	0.20	0.08	50.00%	0.16	Anti-slip
Caustic soda	0.10	0.08	0.03	25.00%	0.13	pH adjuster
Emultex 738	6.53	5.32	2.13	45.00%	4.73	Binder
Viscolam 30	0.03	0.02	0.01	35.00%	0.03	Rheology Modifier
Optiblanc Kln	0.40	0.33	0.13	47.50%	0.27	Optical brightener
TOTALS	122.77	100.00	40.00	40.00%	100.00	

The polyvinyl alcohol was prepared in water at 25% solids at 90°C. The mixture was allowed to cool and a portion of 0.4 parts by weight of the polyvinyl alcohol was added to a portion of 12.2 parts by weights of a 10% magnesium sulfate solution.

A portion of 81 parts by weight of ground calcium carbonate (Setacarb 80 (Trade Mark) supplied by OMYA as a slurry of 76% solids and having an 80% content of particles less than 2 microns and a mean particle size of 0.73 microns) was added to the liquid mixture and it was allowed to stir for 10 minutes.

A portion of 0.2 parts of calcium stearate was added as a lubricant to give the final coating anti-slip properties. To this mixture, a portion of 0.08 parts by weight of caustic soda was added followed by 5.3 parts by weight of Emultex 378. The mix was stirred for 10 minutes and 0.02 parts by weight of Viscolam 30 was added followed by 0.3 parts by weight of Optiblanc KLN. The mix was allowed to stir for 30 minutes, and then coated by blade in a dry solids amount of 5g/m² on top of the previously coated pre-coat layer. This was

followed by a supercalendering process to give a gloss measurement of 46% at 75 degree angle using a Gardner 75° micro-gloss meter.

Example 2

- 5 The following coating mix was prepared in the laboratory showing an ink receiving layer consisting of 85 parts by weight of calcium carbonate (Setacarb 80 (Trade Mark) supplied by OMYA as a slurry of 76% solids and having an 80% content of particles less than 2 microns) and 15 parts by weight of a water based dispersion (a latex) of self cross-linking vinyl acetate homopolymer (Emultex 378 (Trade Mark) supplied by Synthomer
10 Ltd), followed by a non-pigmented layer containing a salt as described in Table III.

Table III

MATERIAL	PARTS DRY	%W/W DRY	DRY WEIGHT / g	SOLIDS	WET Wt / g	Details
WATER					15.93	
MgSO ₄	100.00	71.38	8.57	12.00%	71.38	Divalent salt
PVOH 4-98	28.00	19.99	2.40	25.00%	9.59	Binder
Sterocoll BL	12.00	8.57	1.03	33.30%	3.09	Rheology modifier
Surfynol CT211	0.10	0.07	0.01	100.00%	0.01	Surfactant
TOTALS	140.10	100.00	12.00	12.00%	100.00	

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- The Mowiol 4-98 was prepared in water at 25% solids at 90°C. The mixture was allowed to cool and a portion of 20 parts by weight of the polyvinyl alcohol was added to a portion of 71 parts by weights of a 12% magnesium sulfate solution. 12 parts of an aqueous,
20 anionic solution of an acrylic copolymer was added (Sterocoll Bl (Trade Mark) as supplied by BASF) to adjust the rheology of the mix. The final mixture was coated at 1.5 g/m² by rod on top of the initial coating one side of the substrate sheet.

Example 3

- 25 An ink-receiving layer was applied to one side of a paper sheet as described in Example 1. This was carried out at laboratory scale using scaled-down quantities of materials. The resulting sheet was provided with a further layer of the composition shown in Table IV.

30

Table IV

MATERIAL	PARTS DRY	%W/W DRY	DRY Wt / g	SOLIDS	WET Wt / g
WATER					0.83
Manganese sulfate	6.50	5.69	2.28	5.00%	45.51
Mowiol 4-98	0.46	0.40	0.16	25.00%	0.64
Setacarb 80	100.00	87.52	35.01	74.00%	47.31
Ca stearate	0.25	0.22	0.09	50.00%	0.18
Caustic soda	0.10	0.09	0.04	25.00%	0.14
Emultex 738	6.53	5.71	2.29	45.00%	5.08
Modarez WR/Viscolam 30	0.03	0.02	0.01	35.00%	0.03
Optiblanc KLN	0.40	0.35	0.14	47.50%	0.29
TOTALS	114.27	100.00	40.00	40.00%	100.00

- 5 The polyvinyl alcohol was prepared in water at 25% solids at 90°C. The mixture was allowed to cool and a portion of 0.4 parts by weight of the polyvinyl alcohol was added to a portion of 6 parts by weights of a 5% manganese sulfate solution.

- A portion of 88 parts by weight of Setacarb 80 was added to the liquid mixture and it was
 10 allowed to stir for 10 minutes. A portion of 0.2 parts of calcium stearate was added as a lubricant to give the final coating anti-slip properties. To this mixture, a portion of 0.09 parts by weight of caustic soda was added followed by 6 parts by weight of Emultex 378. The mix was stirred for 10 minutes and 0.02 parts by weight of a Viscolam 30 was added followed by 0.4 parts by weight of optical brightener. The mix was allowed to stir for 30
 15 minutes, and then coated in a dry solids amount of 5g/m² on top of the previously coated pre-coat layer on one side of the substrate sheet.

Example 4

- Samples of paper previously machine coated with a layer of a composition corresponding
 20 to Table I above, prepared as described in Example 1, were provided with a further layer of the composition shown in Table V. This second coating was applied in the laboratory.

Table V

MATERIAL	PARTS DRY	%W/W DRY	DRY Wt / g	SOLIDS	WET Wt / g
WATER					0.33
Magnesium sulfate	15.00	12.50	4.63	10.00%	46.25
HEC (cellosize)	5.00	4.17	1.54	12.00%	12.85
Setacarb 80	100.00	83.33	30.83	76.00%	40.57
TOTALS	120.00	100.00	37.00	37.00%	100.00

Hydroxyethylcellulose (QP-100 MH Cellosize (Trade Mark), a nonionic water-soluble polymer derived from cellulose supplied by Dow Chemical Company Ltd) was prepared in cold water at 12% solids. A portion of 4 parts by weight of the polyvinyl alcohol was
 5 added to a portion of 12.5 parts by weight of a 10% magnesium sulfate solution.

A portion of 83 parts by weight of Setacarb 80 (Trade Mark) was added to the liquid mixture and it was allowed to stir for 10 minutes before being coated in a dry solids amount of 5g/m^2 on top of the previously pre-coated layer.

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Example 5

Samples of paper previously machine coated with a layer of a composition corresponding to Table I above, prepared as described in Example 1, were provided with a further layer of the composition shown in Table VI. This second coating was applied in the laboratory.

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Table VI

MATERIAL	PARTS DRY	%W/W DRY	DRY Wt/ g	SOLIDS	WET Wt / g
WATER					1.03
Magnesium sulfate	15.00	11.28	3.44	10.00%	34.40
Setacarb 80	100.00	75.19	22.93	76.00%	30.17
Mowiol 40-88	18.00	13.53	4.13	12.00%	34.40
TOTALS	133.00	100.00	30.50	30.50%	100.00

20 A portion of 75 parts by weight of Setacarb 80 was added to a portion of 11 parts by weight of a 10% magnesium sulfate solution.

Partially hydrolysed polyvinyl alcohol, Mowiol 40-88 (Trade Mark, manufactured by Kuraray Co., Ltd) was prepared in water at 12% solids at 90°C . The mixture was allowed
 25 to cool and a portion of 13.5 parts by weight of the polyvinyl alcohol was added to the mixture and allowed to stir for 30 minutes. The mix was coated in a dry solids amount of 5g/m^2 on top of the previously pre-coated layer on one side of the substrate sheet.

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Example 6a (comparative)

A paper sheet was coated on one side only at laboratory scale with a simplified version of a typical offset litho recipe. This consisted of 85 parts by weight of calcium carbonate (Setacarb 80 (Trade Mark) supplied by OMYA as a slurry of 76% solids and having an
5 80% content of particles less than 2 microns) and 15 parts by weight of styrene butadiene copolymer Latex, SB 083 (supplied by Latexia). The coat weight was 20gsm.

Example 6b

A similar coating was prepared as Example 6a except that styrene butadiene copolymer
10 Latex, SB 083 was replaced by a water based dispersion (a latex) of self cross-linking vinyl acetate homopolymer (Emultex 378 (Trade Mark) supplied by Synthomer Ltd) and salt (magnesium salt) was added in ratio of 15 parts of salt to 100 parts of pigment.

Example 7

15 A paper sheet was coated on one side only at laboratory scale with a coating mix prepared according to the formulation shown in Example 1, Table II. The coatweight was 20gsm.

Example 8

A paper sheet was coated on one side only at laboratory scale with a coating mix prepared
20 according to the formulation shown in Example 1, Table II, except that the Emultex 378 was replaced by Mowiol 40-88. The coatweight was 20 gsm.

Example 9: Print quality evaluation

The products produced in Examples 1 to 8, together with a conventional product intended
25 for use in an offset litho printer as a comparison (Example 6a) were printed on an inkjet printer (Kodak Easyshare Printer 5300) using water-based inks.

Coated papers intended for printing by offset litho are generally unsuitable for water based ink jet printing. Demanding images such as pink or green text on a trichromatic black
30 background provide a demanding test due to the need to mix a number of inks to produce both the background and foreground colours. This results in a relatively high coverage of the different inks. Therefore this type of image was used in the testing.

The conventional offset paper demonstrated poor absorbance of the ink and irregular wetting of the coating surface. Poor definition of the text, ragged edges to the characters, and bleed of the colours into the surrounding black and vice versa, was observed. This caused the print to be distorted. Also, the distribution of the colour was patchy and uneven.

- 5 In the case of the trichromatic black, this appeared as severe mottle or graininess, as though a black watercolour paint had been applied to polythene and allowed to reticulate as it dried.

The results were quantified on a visual scale by assigning a zero to the comparison product.

- 10 A score of 100 would be given to a perfect print comprising text with vivid, intense colours showing no distortion or bleed, with well defined edges and a background with excellent uniformity of ink coverage and no sign of mottle or graininess. The results are shown in Table VIII. It can be seen that the products made according to the present invention all gave acceptable results, much improved over the comparison product.

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Table VII

Example No.	Gradings
1	85
2	85
3	85
4	70
5	70
6a (comparative)	0 (Severe text bleed and background mottle)
6b	85
7	70
8	70

Example 10a

- 20 A paper sheet was coated on one side with a coating mix prepared according to the formulation shown in Table VIII. Coating weights of 5, 10, 15 and 20g/m² were obtained.

This example contains clay in addition to the main pigment, calcium carbonate. The clay used was a coating grade, KI 1020-2 supplied in slurry form by Kaolin International B.V., containing solids having a mean particle size of 5.04 microns.

5

Table VIII

MATERIAL	PARTS DRY	% W/W DRY	DR WT /g	SOLIDS	WET WT/g
Magnesium sulfate	15.00	11.26	15.00	9.77	153.53
Sodium hydroxide	0.10	0.08	0.10	50.00	0.20
Setacarb 80	80.00	60.11	80.00	75.26	106.30
Kaolin KI 1020	20.00	15.03	20.00	66.42	30.11
Mowiol 40-88	18.00	13.52	18.00	9.97	180.54
TOTALS	133.10	100.00	133.10	28.28	470.68

Example 10b

A coating formulation and coating were prepared as in Example 10a. The Kaolin KI 1020 was replaced by Opacarb A40. This is a precipitated calcium carbonate supplied in slurry form by Speciality Minerals, based in Belgium, containing solids having a mean particle size of 0.62 microns.

Example 10c

A coating formulation and coating were prepared as in Example 10a. The Kaolin KI 1020 was replaced by Kaocal. This is a calcined clay supplied in slurry form by Thiele Kaolin Company of Sandersville, GA, USA., containing solids having a mean particle size of 3.48 microns.

Example 10d (comparative)

This formulation was selected to represent a typical coated paper used in offset litho. It contained 90 parts of Setacarb 80 and 10 parts of Kaolin KI 1020. A styrene butadiene copolymer latex, SB083 (supplied by Latexia) was used as binder at a level of 10 parts. Polyvinyl alcohol, 0.4 parts, was added since this small level is typically used in these coatings to enhance the effectiveness of optical brightening agents. No salt was added.

Example 11: Print quality evaluation

The four coated papers prepared as described in Example 10 were printed using an Epson Stylus D120 inkjet printer using water based inks.

5

The papers containing polyvinyl alcohol as binder and magnesium sulfate gave prints which were dry to the touch as the printed papers emerged from the printer. The coated paper produced according to Example 10d had very poor ink drying properties and the prints could readily be smeared even after a delay of 10 minutes. This would not be

10 acceptable on fast commercial ink jet presses where papers are often two-side printed and wound up in rolls.

The print qualities were good for examples 10a, 10b and 10c. Example 10d showed poor infill of printed lines due to poor wetting of the coating surface by the ink.

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Claims

1. A sheet product comprising a substrate carrying a coating on at least one surface, characterised in that the coating includes (i) a pigment comprising calcium carbonate; (ii) a
5 binder for component (i) comprising a major proportion of a polymer carrying -O-, -CO-,
-OCO- and/or -COO- groups in its side-chains; and (iii) at least at the surface of said
coating, a water-soluble salt of a Group II, Group III or transition metal.
2. A sheet product as claimed in claim 1, in which the pigment comprises a major
10 proportion of calcium carbonate.
3. A sheet product as claimed in claim 2, in which calcium carbonate is the only pigment
present.
- 15 4. A sheet product as claimed in any one of the preceding claims, in which the calcium
carbonate is in the form of ground calcium carbonate.
5. A sheet product as claimed in any one of the preceding claims, in which the pigment has
a mean particle size of 15 microns or less.
20
6. A sheet product as claimed in any one of the preceding claims, in which the pigment has
a mean particle size of greater than 0.2 microns.
7. A sheet product as claimed in any one of the preceding claims, in which the binder
25 comprises at least 80% by weight of a polymer carrying -O-, -CO-, -OCO- and/or -COO-
groups in its side-chains.
8. A sheet product as claimed in any one of the preceding claims, in which the binder
comprises polyvinyl acetate, a vinyl acetate copolymer, polyvinyl alcohol, carboxymethyl
30 cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, sodium alginate, and/or starch.
9. A sheet product as claimed in claim 8, in which the binder comprises polyvinyl acetate.

10. A sheet product as claimed in any one of claims 1 to 9, in which component (iii) comprises a salt of calcium, magnesium, aluminium, manganese or zinc.
11. A sheet product as claimed in claim 10, in which the salt is calcium chloride,
5 manganese sulfate or magnesium sulfate.
12. A sheet product as claimed in claim 11, in which the salt is magnesium sulfate.
13. A sheet product as claimed in any one of the preceding claims, in which the quantity of
10 water-soluble salt present is in the range of from 2 to 35 parts by weight per hundred parts dry weight of calcium carbonate.
14. A sheet product as claimed in claim 13, in which the quantity of water-soluble salt present is in the range of from 5 to 25 parts by weight per hundred parts dry weight of
15 calcium carbonate.
15. A sheet product as claimed in any one of the preceding claims, in which said coating contains two or more separate layers, component (iii) being present in at least the layer furthest away from the surface of the paper substrate.
20
16. A method of printing an image, which comprises applying water-based ink to a sheet product as claimed in any one of claims 1 to 15, using an inkjet printer and a water-based ink.
- 25 17. A method as claimed in claim 16, in which a pigment-based ink is used.
18. The use of a combination of (i) a pigment comprising calcium carbonate; (ii) a binder for component (i) comprising a major proportion of a polymer carrying -O-, -CO-, -OCO- and/or -COO- groups in its side-chains; and (iii) a water-soluble metal salt of a Group II,
30 Group III or transition metal; in a coating for a sheet product, in order to render said sheet product suitable for use in an inkjet printer using a water-based ink.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2009/000282

A. CLASSIFICATION OF SUBJECT MATTER				
INV.	D21H19/36	D21H19/38	D21H19/42	D21H19/44
	D21H19/58	D21H19/60	D21H19/62	D21H19/80
	D21H27/00			D21H19/82
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)				
D21H B41M				
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				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages			Relevant to claim No.
X	DATABASE WPI Week 200764 Thomson Scientific, London, GB; AN 2007-680290 XP002526789 & JP 2007 168378 A (CANON KK) 5 July 2007 (2007-07-05) see [0035], [0056]-[0059], [0074], claims abstract -----			1,8-12, 16-18
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☒ 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 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	
11 May 2009			28/05/2009	
Name and mailing address of the ISA/ European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Koegler-Hoffmann, S	

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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