GOMEZ PINZON & ASOCIADOS

GOMEZ PINZON, LINARES, SAMPER, SUAREZ,
VILLAMIL & ASOCIADOS
ABOGADOS

125

SEÑORA
ALIX CARMENZA CÉSPEDES DE VERGEL
JEFE DE LA DIVISIÓN DE NUEVAS CREACIOI
SUPERINTENDENCIA DE INDUSTRIA Y COME
CIUDAD

SUPERINTENDENCIA Y COMERCIO
Radicacion : 01017435 00000002 Folios: 222
Fecha (AMD): 2001-07-09 16:13:56
Tramite : 002 PATENTES D 1 REGISTRO/ 444 RESPUESTA
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Ref. : **No. de Radicación :** **01017435**
Trámite : **Patente** **002**
Evento : **Registro** **001**
Actuación : **Contestación Requerimiento.**
Patente: **ARAGONITO PRECIPITADO Y UN PROCESO PARA PRODUCIRLO**

MAURICIO JARAMILLO C, abogado en ejercicio, portador de la cédula de ciudadanía número 80'421,942 de Usaquén, y de la Tarjeta Profesional No. 74,555 del Consejo Superior de la Judicatura, actuando en mi carácter de apoderado de la sociedad **3P TECHNOLOGIES LTD,** por medio del presente escrito contesto el requerimiento que me fue notificado a través del Listado de fecha 10 de Mayo de 2001, y que consta en el Auto No. 1396 expedido por esa Superintendencia.

Por medio de este requerimiento se solicita :

- Debe allegar el poder otorgado al abogado que aparece en la solicitud como apoderado, con el lleno de los requisitos exigidos en el Código de Procedimiento Civil. Adicionalmente, deberá presentar el documento que acredita la existencia y representación legal de la sociedad solicitante.

- Debe indicarse el lugar de constitución de la sociedad solicitante.

- Debe allegar copia del documento en que consta la cesión del derecho a la patente otorgado por el inventor al solicitante o su causante.

Al respecto me permito informarle que adjunto a este memorial encontrará :

- Poder debidamente otorgado al Doctor **MAURICIO JARAMILLO C,** abogado en ejercicio, portador de la cédula de ciudadanía número 80'421,942 de Usaquén, y de la Tarjeta Profesional No. 74.555 del Consejo Superior de la Judicatura, identificada con C.C. de No. 51'854.274 de Bogotá y con Tarjeta Profesional No. 56,190, así como a otros abogados de la firma **GOMEZ PINZON & ASOCIADOS.**

- Copia certificada del ministro consejero encargado de las funciones consulares de Colombia en Israel donde consta que ha tenido a la vista los documentos sobre la existencia de la sociedad **3P TECHNOLOGIES LTD,** con registro No, 51-192411-0, con domicilio en Nesher, Israel, y que la citada empresa ejerce actualmente su objeto social conforme a la leyes de Israel.

CARRERA 9 No. 73-24 PISO 3 TELS.(571) 310 70 55/50 66 FAX (571) 310 66 46/57 A.A. 057629
E-MAIL: GOMEZ-PINZON@compuserve.com
SANTA FE DE BOGOTA, D.C.-COLOMBIA

126

- La sociedad solicitante se encuentra constituida en **Nesher, Israel; calle Hata'asia No. 8.**

- Documento de cesión firmado por **ISAAC YANIV** como inventor a la sociedad **3P TECHNOLOGIES LTD.**

Adicionalmente anexamos,

2 cuadernillos que consisten en las solicitudes radicadas en Estados Unidos de América, con el fin de reivindicación de prioridades, los cuales se especifican a continuación:

- **Solicitud No. : 09/519,749**
  Radicada : 6 de Marzo de 2000

- **Solicitud No. : 09/778,920**
  Radicada : 8 de Febrero de 2001

Debido a que en la solicitud colombiana se unieron los conceptos de las solicitudes antes mencionadas, se anexa a este documento:

- **Nuevo resumen del invento, páginas No. 12 a 17**
- **Nuevas páginas 18, 40,63,66,67,70 de la descripción detallada del invento**
- **Nuevo capítulo reivindicatorio, páginas 94 a 109.**

Lo anterior, debido a que se realizaron cambios en la solicitud de registro en Colombia con el fin que quedara en consonancia con las prioridades antes mencionadas.

NOTIFICACIONES

Para efecto de las notificaciones que por disposición del artículo 50 del Decreto 02 de 1984 debe hacer su despacho, informo que mi representado y el suscrito recibiremos las notificaciones en la secretaría de su despacho o en mi oficina de abogados, situada en la carrera 9 # 73-24 de Bogotá D.C., teléfonos 3107055 y 3105066, y fax 3106646.

Cordialmente,

MAURICIO JARAMILLO C.
C.C. 80'421,942 de Usaquén
T.P No. 74,555 del C.S. J

Adjunto : lo anunciado.

3
127

No. 1109

AUTHENTICATION OF SIGNATURE

I the undersigned, Dan Orr, Notary at Haifa, Israel hereby certify that on 19.3.2001 there appeared before me at my office Dr. Isaac Yaniv who is known to me personally, on behalf of the company 3P Technologies Ltd and on his own behalf ,and signed of his own free will the attached document marked "A" (the document overleaf).

In witness whereof I hereby authenticate the signature of the said Signee by my own signature and seal this 19.3.2001.

Notary's seal

דן אור
עורך-דין ונוטריון
שד' מוריה 20, חיפה

signature

Dan Orr

APOSTILLE

(Convention de la Haye du 5 Octobre 1961)

1. **STATE OF ISRAEL** — 1. מדינת ישראל
This public document — מסמך ציבורי זה
2. Has been signed by — 2. נחתם בידי

_____ Advocate — עו"ד 01/12

3. acting in capacity of Notary — 3. המכהן בתור נוטריון
4. bears the seal/stamp of the above Notary — 4. נושא את חותם / חותמת של נוטריון הנ"ל

Certified — **אושר**

5. at the Ministry of Justice, Jerusalem — 5. במשרד המשפטים בירושלים
6. by an official appointed by the Minister of Justice under the Notaries Law, 1976 — 6. על ידי מי שמונה בידי שר המשפטים לפי חוק הנוטריונים, תשל"ו-1976

7. Serial number _____ — 7. מס' סידורי _____
8. Seal/Stamp — 8. חותם / חותמת
9. Signature _____ — 9. חתימה _____
10. Date _____ — 10. ביום

24 APR 2001

CONSULADO DE COLOMBIA

CONSULADO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

29 MAY 2001

JUAN MANUEL SOTERO MEDINA
CONSUL

A 729

POWER WITH ASSIGNMENT - Patents
PODER CON CESION - Patentes

The undersigned / abajo firmante(s) (1) Isaac Yaniv

residing at / domiciliado(s) en 75 Yaqinton Street, Haifa 34792 Israel

declare(s) that by these presents grant / declara(n) por la presente otorgar a: UNION ANDINA DE PATENTES S.A.C. (Ltda

special power to apply for and obtain from the competent offices and authorities of / poder especial para solicitar y obtener de las oficinas y autoridades competentes de: Colombia;

Letters Patent for / Patente de invención por PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT

to be issued in the name of / cuyo título deberá extenderse a nombre de (2) 3P. Technologies Ltd.

residing at / domiciliado en P.O. Box 155, Nesher 36802 Israel

to whom assignment has been made of all rights and title to the said invention in the territory of / a quien ha concedido todos derechos de la expresada invención para el territorio de Colombia

the consideration for the said assignment being the sum of / mediante el precio de _____

receipt whereof is hereby acknowledged / que declara haber recibido.

CUMPLE CON EL ORIGINAL QUE REPOSA EN ESTE DESPACHO. BOGOTA, [illegible]

The assignee signs also as evidence of acceptance of the aforesaid assignment and authorizes the above named attorneys so that any of them, acting jointly or individually, may undertake the required proceedings before the corresponding offices and authorities, such as petitions, declarations, amendments, appeals, answer oppositions, pay official fees, charges and in general make any payments that may be required by law and to recover same if necessary; receive any kind of documents and securities and issue the corresponding receipts; abandon, collect and in general, effect all necessary actions for the proper execution of this commission. The attorneys are expressly authorized to file and prosecute oppositions against third parties' applications that may harm the rights of the inventor(s) or of the assignee, and may carry out any legal actions to that effect. This power may be delegated and reassumed as many times as considered necessary by the attorneys

El cesionario también firma en señal de aceptación de la cesión y faculta a los supradichos apoderados para que cualquiera de ellos, actuando conjunta o individualmente, puedan realizar ante dichas [illegible] las gestiones necesarias para el objeto señalado, tales como presentar solicitudes, declaraciones, enmiendas y apelaciones, contestar oposiciones; efectuar pagos de impuestos y costas y en general todos los pagos requeridos por la ley y recobrar los mismos en caso necesario, recibir toda clase de documentos y títulos y otorgar los correspondientes recibos, desistir, percibir y en general, [illegible] los actos necesarios en el cabal desempeño del mandato. Los apoderados quedan expresamente facultados para deducir y transitar oposiciones contra solicitudes de terceros que puedan afectar los derechos del (de los) inventor (es) o del cesionario, pudiendo ejercer el efecto todos los recursos legales. El presente poder puede ser delegado y reasumido cuantas veces lo estimen necesario los apoderados

Signed in / Firmado en Herzlia ISRAEL Date / Fecha 15 March 2001

(1) I. Yaniv
Signature of Inventor
Firma del Inventor

(2) 3 P Technologies Ltd.
Signature of the Assignee
Firma del Cesionario

No. 1114

16
130

AUTHENTICATION OF SIGNATURE

I the undersigned, Dan Orr, Notary at Haifa, Israel hereby certify that on 10.4.2001 there appeared before me at my office Dr. Isaac Yaniv who is known to me personally, and signed of his own free will the attached document marked "A" (the document overleaf).

In witness whereof I hereby authenticate the signature of the said Signee by my own signature and seal this 10.4.2001.

Notary's seal

signature

Dan Orr

DE BOGOTÁ, HAGO CONSTAR QUE ESTA COPIA FOTOSTÁTICA CONCUERDA CON EL ORIGINAL QUE ME TENGO A LA VISTA

29 MAY 2001

JUAN MANUEL ROTERO MARTINEZ
NOTARIO

APOSTILLE

(Convention de la Haye du 5 Octobre 1961)

1. STATE OF ISRAEL — 1. מדינת ישראל

This public document — מסמך ציבורי זה

2. Has been signed by — 2. נחתם בידי

_____ Advocate — עו"ד _____

3. acting in capacity of Notary — 3. המכהן בתור נוטריון

4. bears the seal/stamp of the above Notary — 4. נושא את חותמם / חותמת של נוטריון חנ"ל

Certified — **אושר**

5. at the Ministry of Justice, Jerusalem — 5. במשרד המשפטים בירושלים

6. by an official appointed by the Minister of Justice under the Notaries Law, 1976 — 6. על ידי מי שמונה בידי שר המשפטים לפי חוק הנוטריונים, תשל"ו-1976

7. Serial number _____ — 7. מס' סידורי _____

8. Seal/Stamp — 8. חותמם / חותמת

9. Signature _____ — 9. חתימה _____

10. Date _____ — 10. ביום

24 APR 2001

משרד המשפטים MINISTRY OF JUSTICE

(COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE ME FUERON A LA VISTA

29 MAY 2001

JUAN MANUEL GUTIERREZ MEDINA
NOTARIO

132

POWER OF ATTORNEY

Be it known that

3P.TECHNOLOGIES LTD.

of P.O.Box 155, Nesher 36602, Israel.

do hereby grant to :

Eurocia Angulo Rabanal and / or
Mauricio Jaramillo Campuzano and/or
Patricia Arrazola Bustillo and/or
Paula Samper Salazar and / or
José Luis Suarez Parra

full and sufficient power of attorney so that each person, individually, may apply before the appropriate national offices and authorities, for the application and issuance of patents, precautelatory patents, registration of trademarks and service marks, registration of industrial designs and utility models, commercial names, commercial slogans, collective marks, sanitary registrations, sanitary licenses, Internet Domain Names and protection of industrial secrets or know-how as well as any other element of Industrial Property and Copyright recognized by the legislation of the **Republic of Colombia**, being empowered to take all necessary steps before the said authorities for the objects stated above, including, without limiting to, filing petitions, making declarations, paying taxes, paying administrative fees, ordering the publications and notices as required by law, receiving letter patents, titles and certificates, filing observations or oppositions to applications filed by third parties, apply for cancellation or nullity of Industrial Property rights in the name of third parties, to withdraw such actions and celebrate transactions, to answer oppositions, observations, cancellation and nullity actions filed and celebrate transactional agreements, to request recordal

PODER

Conste que

3P. TECHNOLOGIES LTD.

domiciliado en P.O.Box 155, Nesher 36602,

Israel.

por el presente otorga a :

Eurocia Angulo Rabanal y / o
Mauricio Jaramillo Campuzano y/o
Patricia Arrazola Bustillo y/o
Paula Samper Salazar y/o
José Luis Suarez Parra

29 MAY 2001

indistintamente, poder amplio y suficiente para solicitar, gestionar, obtener y recabar de las oficinas y autoridades nacionales que corresponda, la obtención de patentes de invención, registros de marcas, registros de diseños industriales y modelos de utilidad, nombres comerciales, lemas comerciales, marcas colectivas, registros sanitarios, licencias sanitarias de funcionamiento nombres de dominio de Internet y la protección de secretos industriales, y, en general, cualquier elemento de Propiedad Industrial y Derechos de Autor reconocido por la legislación de la **República de Colombia**, facultándoles de manera expresa para dar ante dichas autoridades todos los pasos necesarios incluyendo, sin limitación, el preparar y presentar solicitudes, hacer declaraciones, pagar tasas, contribuciones e impuestos, ordenar las publicaciones de ley, recabar los títulos o certificados, formular observaciones a solicitudes de registro presentadas por terceros, deducir oposiciones, interponer recursos de cancelación y nulidad de Derechos de Propiedad Industrial de propiedad de terceros, desistirse de los mismos y celebrar convenios transaccionales, incluyendo el

transactional agreements, to request recordal of licenses, assignments, mergers, changes of name and, in general any agreement which will modify the records of a particular registration, to accept assignments of Industrial Property elements that third parties perform on our behalf, sign for such purposes the appropriate agreements, including arbitration clauses, to apply for amendments on the description of goods and services included in pending applications, registered marks on the time of renewal of the particular registration, including, as a consequence of an agreement with a third party, the extension or limitation of goods or services, to prepare and file actions for violation of the law of unfair competition and of infringements of Industrial Property rights and Copyrights, including legislation of the Advertising Legislation and Consumer Protection before the appropriate authorities, with all sufficient powers required for the appropriate action, including the request of inspections, to appoint and accept appointment of examiners, to conduct preparatory proceeding, offer evidence, to answer infringements, unfair competition actions and actions for violation of Advertising Legislation filed by third parties against our company, with full power to represent in the whole administrative procedure, to defend petitions for cancellation of registrations and declare the voidness of administrative resolutions. They are also empowered to appeal, request reconsideration of resolutions and request the voidness of resolutions, to request declarations, prove working, withdraw applications. They are also empowered to file civil and constitutional actions, including court actions seeking reversal of administrative resolutions, and to defend actions initiated against our company, with all such powers as may be required including to make arrangements, submit to arbitrators, request declarations and testimonies, to desist, to collect to collect and to appeal, to file actions against the Criminal Courts, to appeal and celebrate transaction agreements.

arbitraje, contestar oposiciones, observaciones, nulidades y cancelaciones formuladas por terceros y celebrar con estos convenios transaccionales, solicitar la inscripción de licencias, transferencias, cambios de nombre, fusiones y, en general, de todo acto modificatorio de registro, aceptar transferencias que terceros hagan en favor del poderdante, suscribiendo, para tal efecto, los contratos correspondientes, incluyendo cláusulas de sometimiento a arbitraje, solicitar modificaciones a la descripción de productos o servicios a registros de marca de producto o de servicio, incluyendo la de extensión y la de limitación durante el trámite de registro, expedido éste o al momento de su renovación, interponer acciones por violación de las normas de represión de la competencia desleal, de infracción de derechos de Propiedad Industrial y Derechos de Autor, denuncias por violación de normas de Publicidad Comercial y Protección al Consumidor ante cualquier organismo competente, con todas las facultades requeridas para el trámite correspondiente, incluyendo la de solicitar inspecciones, nombrar y aceptar el nombramiento de peritos, conducir diligencias preparatorias, solicitar, aportar y presentar pruebas, contestar acciones de infracción, denuncias de competencia desleal y de violación de Normas de Publicidad Comercial y de Protección al Consumidor formuladas por terceros contra el poderdante, representándolo durante todo el procedimiento administrativo o judicial correspondiente, defender acciones de cancelación de registro y nulidades de resoluciones administrativas. Quedan igualmente facultados para interponer todo tipo de recursos impugnativos, incluyendo reconsideraciones, apelaciones y nulidades, solicitar declaraciones testimoniales, probar explotaciones, formular desistimientos, interponer reclamos. Asimismo, quedan facultados para interponer acciones judiciales y contencioso administrativas de nulidad de resoluciones administrativas, y para representarnos como demandados en acciones

3 P Technol

This document expressly ratifies all applications, acts or petitions that the above-mentioned persons have conducted in our name regarding any Industrial Property matter and/or Copyright which has been conducted before the issuance and signature of this document. The agents will also have the right to substitute these powers completely or partially in other attorneys of the law firm ....
....
and to revoke such substitutions.

Given and signed on ...10.... APRIL ...2001...........

....
.....3 P Technologies Ltd.............................
....

civiles y constitucionales de toda índole, incluyendo la defensa en acciones de nulidad de resoluciones administrativas interpuestas por terceros, incluyendo las facultades de transacción, sometimiento a arbitraje, solicitar declaraciones y confesiones, desistirse percibir; interponer o formular denuncias ante la Jurisdicción Penal por delitos contra la Propiedad Industrial y la Propiedad Intelectual respecto de actos de infracción cometidos por terceros en contra de derechos de la poderdante, con facultades para comparecer en el proceso como parte civil, con facultades para interponer recursos y de celebrar acuerdos transaccionales.

Por el presente documento ratifico lo actuado por los apoderados arriba mencionados a nombre de la sociedad antes de la fecha de otorgamiento del presente poder, y desde ahora declaro válido y bueno todo cuanto los apoderados hicieren en nuestro beneficio.

Este poder comprende la facultad de ratificar o confirmar, en nuestro nombre, lo actuado, así como la facultad de recibir, desistir, transigir, comprometer, y de sustituir el presente poder en todo o en parte a otros abogados de la firma ....
....
y de revocar dichas sustituciones.

Otorgado y firmado el
....
....
....
....

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA
29 MAY 2001
JUAN MANUEL BOTERO MEDINA
NOTARIO

Acepto,

NOTARIA SEXTA DE BOGOTA
RECONOCIMIENTO Y PRESENTACION PERSONAL

Santafé de Bogotá D. C. 29 MAYO 2001
Ante Mi JUAN MANUEL BOTERO MEDINA
NOTARIO SEXTO DEL CIRCULO DE BOGOTA
Comparecio(eron) [illegible]

quien(es) exhibió(eron) la(s) C. C. [illegible]

y dentro Legitimado(s) manifestó(aron) [illegible]

domiciliado(s) en Bogotá, y declaró(aron) que la(s) firma(s) que aparece(n) en el presente documento es(son) la(s) suya(s) y que el contenido del mismo es cierto.

En constancia se firma esta diligencia, y se imprime huella dactilar

JUAN MANUEL BOTERO MEDINA
NOTARIO

DESPACHO NOTARIAL SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA. HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA
29 MAY 2001
JUAN MANUEL BOTERO MEDINA
NOTARIO

REPUBLICA DE COLOMBIA
SANTAFE DE BOGOTA D.C.

135

CONSULADO DE COLOMBIA

No. 071

EL SUSCRITO MINISTRO CONSEJERO ENCARGADO DE LAS FUNCIONES CONSULARES DE COLOMBIA EN ISRAEL

C E R T I F I C A

- **Que ha tenido a la vista los documentos sobre la existencia de 3 P TECHNOLOGIES LTD., con Registro No. 51-192411-0 de la Oficina de Registro Israelí de Compañías de fecha 22 de Agosto de 1999 , con domicilio en la calle Hata'asia No 8, Nesher, Israel, y que la citada Empresa ejerce actualmente su objeto social conforme a las leyes del Estado de Israel.**
- **Que el doctor ITZHAK YANIV en su calidad de Presidente es representante legal de la Compañía y como tal está autorizado para firmar el documento que antecede.**
- **El Cónsul no asume responsabilidad alguna por el contenido del documento.**
- **La presente Certificación se otorga a solicitud de la parte interesada en Tel Aviv, a los veinticinco días del mes de Abril del año 2001.**

CONSULADO DE COLOMBIA * TEL-AVIV *

CAYO AUGUSTO TOVAR SANCHEZ
Ministro Consejero
Encargado de las Funciones Consulares

CUPO NOTARIAL SEXTO (6°) CIRCUITO DE BARRANQUILLA DE BOGOTA. HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA
29 MAY 2001
JUAN MANUEL BOTERO MEDINA
NOTARIO

DERECHOS CANCELADOS:
UsS 107.-

RESUMEN DEL INVENTO

Sorpresivamente se ha hallado de acuerdo con el invento actual, el carbonato de calcio precipitado particular, y particularmente carbonato de calcio de aragonito precipitado particular , que es caracterizado por su alta blancura, alto índice refractor efectivo, densidad baja en grandes cantidades (aparentemente (suelto) densidad mayor (L.B.D.) y densidad mayor captada (T.B:D.) y especialmente por su gravedad específica escasa (inferior a los 2,5 g/cm^3), puede ser producido, y que los objetivos anteriormente mencionados del invento actual pueden ser logrados, por un proceso que comprende reacciones de una mezcla de hidróxido de calcio acuosa con un gas seleccionado del dióxido de carbono y un gas que lo contenga, en donde los parámetros del proceso, incluyendo por ejemplo, por lo menos un agente activo preseleccionado, modos de operación, concentraciones de operación de materias primas, temperaturas de operación, orden de operación, PH y velocidades de mezcla de alto corte, son estrictamente controlados de tal forma que el producto deseado sea obtenido. En una específica incorporación, el lanzamiento del producto ocurre durante este proceso.

En consecuencia, el presente invento, proporciona un incorporación particular, un proceso para la producción de carbonato de calcio aragonito precipitado particularmente y el particular carbonato de calcio aragonito precipitado así producido, cuyo proceso comprende una reacción de mezcla de hidróxido de calcio acuosa con un gas seleccionado del grupo consistente de dióxido de carbono y un gas que lo contiene, donde los parámetros de dichos procesos por lo menos incluyen un agente activo preseleccionado, un modo de operación, concentraciones de operaciones de materia prima, temperatura de operación, velocidad de la mezcladora en la operación y operaciones PH , tales, por lo menos uno de los siguientes criterios (a), (b) y (c) cumplen:

(a) la gravedad específica del producto después del secado por 12 horas a 120°C es < 2,5 g/cm^3 y la gravedad específica de este producto seco después del encendido por 8 horas a 500°C es < 2,5 g/cm^3.

(b) la densidad mayor aparente (suelto) del producto después del secado por 12 horas a 120°C es <0,50 g/cm^3.

(c)la densidad mayor captada (T.B.D.) del producto después del secado por 12 horas a 120°C es<0,70g/cm^3.

Preferiblemente el producto cumple por lo menos con unos de los siguientes criterios:

(a) Éste tiene una gravedad específica <2,3 g/cm^3 después del secado a 120°C, y una gravedad específica <2,3 g/cm^3 después del encendido por 8 horas a 500°C del producto fundido.

(b) Este tiene un L.B.D. <0,45 g/cm^3 después del secado a 120 °C por 12 horas.

(c) Este tiene un T.B.D. <0,60g/cm^3 después del secado a 120°C por 12 horas.

Mucho mas preferiblemente, el productosatisface por lo menos con uno de los siguientes criterios:

(a) Tiene una gravedad especifica <2.1g/cm3 despues del secado a 120° C, y una gravedad especifica de < 2.1g/cm3 despues del encendido por 8 horas a 500° C del producto thus-fried.
(b) Este tiene un L.B.D. <0.40 g/cm3, después del secado a 120° C por 12 horas.
(c) Este tiene un T.B.D. <0.55 g/cm3, después del secado a 120° C por 12 horas.

Mas allá de la incorporación del invento, existe un proceso proporcionado para la producción del carbonato de calcio de aragonito precipitado particular, y el particular carbonato de calcio aragonito particular así producido, cuyo proceso comprende la reacción de una mezcla de hidróxido de calcio acuosa con un gas seleccionado del grupo consistente de dióxido de carbono y un gas que lo contiene, donde lo parámetros de dichos procesos incluyen por lo menos un agente activo preseleccionado, modo de operación, concentraciones de operaciones de materias primas, temperaturas de operación, operación de velocidad de la mezcladora y operaciones PH, donde por lo menos dicho agente sea seleccionado del ácido nonanoico, ácido decanoico, ácido undecanoico, ácido dodecanoico, ácido tetra decanoico, ácido octadecanoico y ácido undecilenico, cuyas sales carboxylato, cuyos ácidos anhídridos, cuyos ésteres, cuyos halidos acilos y sus quetonas.

El proceso del invento para producir una aragonita precipitada particular de acuerdo con el invento, es en forma adicional preferiblemente caracterizado por lo menos uno, y preferiblemente todos, de las siguientes características: (a) el agente activo involucra por lo menos uno de los miembros seleccionados del grupo consistentes en ácidos cárboxílicos de formula RCOOH, donde el grupo orgánico R (los cuales podrían ser por ejemplo un grupo alfático saturado o no saturado, tales como el grupo hidrocarbono que podría ser sustituido o no sustituido) contiene de 7-20 átomos de carbono, y sus sales carboxilatos, ésteres, anhidridos, hálidos acilos, y sus quetonas (b) más especificamente, el agente activo comprende por lo menos un miembro seleccionado del grupo consistente de ácidos carboxílicos de formula $C_nH_{2n+1}COOH$, donde n es 8-17, y sus sales carboxilatos, ésteres, anhidridos, hálidos acilos y sus quetonas; (c) también, el agente activo comprende por lo menos un miembro seleccionado del grupo consistente de ácidos carboxílicos de fórmula $C_nH_{2n-1}COOH$, donde n es 8-17, y sus sales carboxilatos, ésteres, anhídridos, hálidos acilos, y sus quetonas; (d) más específicamente, el agente activo comprende por lo menos un miembro seleccionado del grupo consistente de ácidos carboxílicos de fórmula $CH_3(CH_2)_nCOOH$, donde n es 7-16, y sus sales carboxilatos, ésteres, anhídridos, hálidos acilos y sus quetonas de fórmula $CH_3(CH_2)_{n-1}C=C=O$; (e) la concentración del agente activo se encuentra dentro del orden de entre 0,2 wt.% y 10 wt.%, calculado como RCOOH y basado en el peso del carbonato de calcio; (f) la mezcla contiene hidróxido de calcio en una concentración dentro del orden del 3 al 30 wt.%, más preferiblemente de 4 a 20 wt.%; (g) el producto es producido en un pH entre 8 y 11, preferiblemente entre 9 y 10; (h) el proceso se efectúa en una temperatura del orden entre los 60°C, preferiblemente entre los 80°C, y la temperatura de ebullición de la combinación de la reacción; (i) el proceso se realiza ya sea en un modo de operación semi-contínua (intermitente), modo de operación, o más preferiblemente de forma contínua;. (j) el proceso se realiza bajo una combinación de alto corte por ejemplo con un mezclador que involucra una armazón/rotor o un rotor únicamente, la velocidad periférica del motor (punta) será de preferentemente de por los menos 5 m/seg. Dentro de una incorporación específica, el proceso se realiza en un modo continuo de operación bajo combinación de alto corte combinando con un velocidad periférica del mezclador (punta) que involucra un rotor/ armazón o un rotor únicamente, en una temperatura del orden entre 90°C y la temperatura de ebullición de la combinación del agente activo – preferiblemente presente en una cantidad del orden entre 0,2%

y 10wt% estimado sobre el peso del carbonato de calcio – que es seleccionado de los ácidos carboxílicos y sus sales de calcio, y la mezcla contiene hidróxido de calcio en una concentración en el orden del 5 a 15 wt.%, el agente activo es preferentemente premezclado con la mezcla del hidróxido de calcio previa a la reacción del dióxido de carbono.

El invento actual también proporciona una novedosa sustancia química – que resulta por supuesto asequible con el proceso actual, un aragonito precipitado particular, que tiene una gravedad específica de <2,5 g/cm^3 (preferiblemente <2,3 g/cm^3, más preferentemente <2,0 g/cm^3, incluso más preferentemente <1,5 g/cm^3) después de secado en 120°C, y una gravedad específica <2,5 g/cm^3 (preferiblemente <2,3 g/cm^3, incluso más preferentemente <2,1 g/cm^3) después del encendido por 8 hr en 500°C. En una incorporación específica, el producto tiene una gravedad específica de 2,3 g/cm^3 después de secado en 120°C, y una gravedad específica de <2,3 g/cm^3 después del encendido por 8 hr en 500°C y en otra incorporación específica, el producto tiene una gravedad específica de <2,1 g/cm^3 después de secado en 120°C, y una gravedad específica de <2,1 g/cm^3 después del encendido durante 8 hr en 500°C.

Un producto así de típico podría ser caracterizado en por lo menos una de las siguientes características: contiene las mencionadas sales de calcio de ácido carboxílico en una cantidad entre 0,2 y 10 wt.%, estimado como $CH_3(CH_2)_nCOOH$ y en base al peso del carbonato de calcio; este tiene una gravedad específica de <2,2 g/cm^3, preferiblemente de <2,0 g/cm^3, más preferiblemente de <1,8 g/cm^3, e incluso más preferiblemente de <1,5 g/cm^3; un producto previamente secado en 120°C por 12 hr tiene una pérdida en el secado de 300°C durante 8 hr de alrededor de <10% wt %, en base al peso del carbonato de calcio; un producto previamente secado en 120°C durante 12 hr tiene un encendido de 500°C durante 8 hr de alrededor de <10% wt.%, en base al peso del carbonato de calcio; después del secado en 120°C durante 12 hr, y/o secado durante 8 hr en 300°C, y/o de combustible por 8 hr en 500°C, esto tiene una gravedad específica de < 2,5 g/cm^3; después del secado en 120°C durante 12 hr, y/o secado durante 8 hr en 300°C, y/o combustible durante 8 hr a 500°C. El producto es además caracterizado por su densidad baja en grandes cantidades y en particular una aparente densidad en cantidades (suelto) debajo del 0,50

(preferiblemente <0,45, más preferible <0,40) g/cm^3 y una densidad de cantidad mayor captada debejo de 0,70(preferiblemente <0,60, más preferible <0,55) g/cm^3.

En otro aspecto, el presente invento provee un araganito precipitado particular que contiene por lo menos una sal cálcica de ácidos carboxílicos seleccionados de la fórmula general: $C_nH_{2n\pm1}COOH$, en donde n = 8-17, en una cantidad entre 0,2 y 10 wt.%, estimada como $C_nH_{2n\pm1}COOH$ y en base al peso del carbonato de calcio, y que tiene (A) una gravedad específica de <2,5 g/cm^3 después de secado durante 12 hr a 120°C, y/o (B) una gravedad específica de <2,5 g/cm^3 después del encendido durante 8 hr a 500°C del producto secado, preferentemente en (A).

En otro aspecto, el invento actual proporciona un aragonito precipitado particular que contiene por lo menos una sal cálcica de ácidos carboxílicos seleccionados de la formula general: $CH_3(CH_2)_nCOOH$, en donde n = 7-16, en una cantidad entre 0,2 y 10 wt.%, estimado como $CH_3(CH_2)_nCOOH$ y en base al peso del carbonato de calcio, y que tiene (A) una gravedad específica de <2,5 g/cm^3 después del secado durante 12 hr a 120°C, y/o (B) una gravedad específica de <2,5 g/cm^3 después del encendido durante 8 hr a 500°C del producto secado, preferentemente en (A).

En aún otro aspecto, el invento actual proporciona un aragonito precipitado particular que contiene por lo menos una sal cálcica de ácidos carboxílicos seleccionada de ácido nonanoico, ácido decanoico, ácido undecanoico, ácido dodecanoico, ácido tetradecanoico, ácido octadecanoico y ácido undeciclénico en una cantidad entre 0,2 y 10 wt.% estimado como $CH_3(CH_2)_nCOOH$ y en base al peso del carbonato de calcio, y que tiene (A) una gravedad específica de <2,5 g/cm^3 después de secado durante 12 hr a 120°C, y/o (B) una gravedad específica de <2,5 g/cm^3 después del encendido durante 8 hr a 500°C del producto secado, preferentemente en (A).

El producto del invento actual puede ser utilizado como un constructor, un material antibloque, un encapsulante, un absorbente, un material de engrosamiento, un protector del sol, un relleno, un extensor y en forma particular como un pigmento para el detergente, productos farmacéuticos, agroquímicos, plásticos, adhesivos, imprenta, cobertura (pintura), papel, jebe, filtración, productos de higiene y muchas otras industrias. De ahí que, de acuerdo con aspectos adicionales del

invento actual se proporciona una composición de cobertura, una composición de papel, una composición plástica, una composición de jebe, una composición absorbente, una composición de detergente en polvo, una composición farmacéutica, una composición agroquímica, una composición de sabor, una composición de fragancia y una composición de protector del sol, cada una involucra un aragonito precipitado particular de acuerdo con el invento. Para dicho propósito, tales composiciones podrían involucrar, por ejemplo aragonito precipitado particular sustancialmente seco, o aragonito precipitado particular en dispersión acuosa.

El PCC del presente invento puede ser utilizado en la mayoría de los productos (consumidor) que el arte previo del carbonato de calcio particular es usado (y posiblemente en todos ellos). Sin embargo, el PCC del invento actual mostrará sus ventajas y propiedades únicas cuando estos productos (consumidor) sean producidos y/o sean utilizados bajo condiciones que exploten su naturaleza porosa como un absorbente para líquidos (por ejemplo en polvos o detergentes en polvo, en productos farmacéuticos, agroquímicos y en varios productos domésticos como alimentos y formulas de alimentación. También, como un agente encapsulante para sabores y fragancias, productos farmacéuticos y agroquímicos) y/o un agente antibloque (e.g en polvos o detergentes en polvo, en productos farmacéuticos agroquímicos y en productos domésticos como alimentos y formulas de alimentación) como un componente "light" (liviano) para reducir la densidad de peso de los productos (por ejemplo, cuando es utilizado como relleno y/o constructor en polvos o detergentes en polvo), como material engrosante (por ejemplo, en gomas, sellantes, adhesivos, coberturas(pinturas), y en papel), como relleno, como un extensor y, particularmente, como un pigmento (por ejemplo en fórmulas de protectores solares, plásticos, adhesivos, imprenta (tintas), coberturas (pinturas), papel (especialmente fórmulas para papel de cobertura, y particularmente para productos de papel de alto brillo), jebe, filtración y muchos otros).

DESCRIPCION BREVE DE LAS FIGURAS.

La Figura 1 muestra una hoja esquemática para la producción de carbonato de calcio precipitado particular de acuerdo al arte previo.

La Figura 2 muestra una hoja esquemática para la producción de aragonito precipitado particular de acuerdo con una incorporación del invento actual.
La Figura 3 muestra una sección esquemática vertical, una celda de reacción/flotación para la producción de aragonito precipitado particular de acuerdo con una incorporación del invento actual.
La Figura 4 muestra un dibujo SEM de un aragonito precipitado particular sustancialmente puro de acuerdo con una incorporación del invento actual.
La Figura 5 muestra un espectro XRD de un aragonito precipitado particular sustancialmente puro de acuerdo con una incorporación del invento actual.
La Figura 6 muestra un dibujo SEM de ARP-76, un aragonito precipitado particular sustancialmente puro de acuerdo con una incorporación del invento actual.
La Figura 7 muestra un espectro XRD de ARP 76, un aragonito precipitado particular sustancialmente puro de acuerdo con una incorporación del invento actual.
La Figura 8 muestra un dibujo SEM ARP-70, una combinación de ~50% de un aragonito precipitado particular y ~50% de calcita precipitada particular, de acuerdo con una incorporación del invento actual.
La Figura 9 muestra un espectro XRD de ARP-70, una combinación de ~50% de aragonito precipitado particular y ~50% de calcita precipitada particular de acuerdo con una incorporación del invento actual.

DESCRIPCION DETALLADA DEL INVENTO.

En el proceso del invento actual, una mezcla de hidróxido de calcio en agua y gas de dióxido de carbono o dióxido de carbono que contiene gas es reaccionado junto en la presencia del agente activo bajo las condiciones astringentes de proceso, para generar un aragonito precipitado particular que tenga propiedades únicas.

El producto del invento actual se caracteriza por bajo costo de producción y por sus propiedades físicas únicas (alta blancura, índice refractor de alta efectividad (<2,5g/cm^3)) al menos una de y preferentemente todos de bajo L.B.D. (<0,50g/cm^3), bajo T.B.D. (<0,70g/cm^3) y gravedad especifica baja (<2,5g/cm^3), y por sus excelentes propiedades químicas (hidrofobicidad y ácidos débiles), lo que se vuelve particularmente adecuado con un absorbente de líquidos, un material

cuando se analiza el producto del invento actual, y seguir las instrucciones de como hacerlo (ver en el Ejemplo 14 y especialmente en el Ejemplo 14 (E)). Estas medidas revelan mejor las propiedades deseadas de los productos novedosos del invento actual y del proceso del invento actual y dan una imagen cercana de cómo estas partículas PCC están orientadas a mejorar los productos finales (consumidor), debido a su única propiedad – "porosidad".

Densidad del Peso (L.B.D. y/o T.B.D.)

Se puede hacer otra observación en base a información experimental recolectada hasta el momento, que la densidad del peso (L.B.D. y/o T.B.D.) de los productos del invento actual tienen valores profundamente inferiores (L.B.D. < 0,50 g/cm^3 e incluso <0,40 g/cm^3 y/o T.B.D. < 0,70 g/cm^3 e incluso <0,60 g/cm^3), que aquellos de productos similares del arte previo (que usualmente tienen L.B.D. >0,5 g/cm^3 y T.B.D. >0,7 g/cm^3). De ahí que, podríamos utilizar estos criterios de alternativa, es decir L.B.D. y/o T.B.D., para indicar si un producto se encuentra dentro del dominio del invento actual. Un procedimiento modelo de cómo realizar estas pruebas se detallará en el Ejemplo 14, partes (F) Y (G) respectivamente.

En forma general, los productos PCC particulares, previamente secados a 120°C durante doce horas, que son de SSA (Area de Superficie Específica) (BET) ≤ 15 m^2/g pertenecerá al dominio del invento actual por ejemplo en las incorporaciones unidas a la densidad del peso y/o consideraciones S.G., si tienen un L.B.D. de menos de 0,55 g/cm^3 y/o un T.B.D. de menos de 0,70 g/cm^3 y de otra forma cumplir con las definiciones mencionadas en estas reivindicaciones. Los productos de SSA más altos en general no serán evaluados para L.B.D. y/o T.B.D., pero sólo para la prueba S.G., como se instruyó en el ejemplo 14 (E).

El invento actual describirá ahora en mayor detalle por medio de ejemplo, que son presentadas para fines de ilustración solamente y no son interpretadas restrictivamente.

2. La muestra seca fue calcinada por8 horas a 500°C. La pérdida sobre el encendido (L.O.I.) se determinó después.
3. El S:G del polvo calcinado fue medido de la forma anterior.
4. La densidad del polvo suelto (B.D.) del polvo secofue medido utilizando una balanza y un cilindro graduado (c.f.) el procedimiento exacto en el EJEMPLO 14 (F). Los resultados los siguientes:

Prueba #	Código de Muestra	Dosis %(wt)	L.O.I. %(wt) 500°C^^	S.G.† g/cm³	B.D.† Suelto g/cm³
19	Natural $CaCO_3$	-	0,18	2,70	0,75
20	BM-37	1*	2,58	2,60	0,38
21	C**	N.A.	2,02	2,71	0,55
22	AR-81	0.5	1,32	2,13	0,23
23	AR-83	1	1,44	2,03	0,22
24	AR-118	2	2,07	2,01	0,18
25	AR-119	5***	5,25	1,93	0,19
26	AR-135	1	1,44	2,01	0,24
27	AR-120	2^	2,37	1,91	0,18

* - La muestra fue tomada del modo grupal de operación en – EJEMPLO 3.

** - PCC Comercial- Aragonito; de Specialty Minerals Inc. (SMI); Opacarb® A40.

*** - 5g of AR-119 fueron disueltos en una solución de HCl al 10%. No se detectó, ni se extrajo ningún ácido, como se esperaba de dichas moléculas cuando ellas fueron sometidas al calor durante 8 horas a 500°C.

^ - 50ppm de ácido fosfórico fueron utilizados adicionalmente al ácido decanoico.

^^ - El Aragonito se convierte en calcita a T > 400°C.

† - Un polvo seco después del secado por 12 horas a 120°C y en adelante un calentamiento de 8 horas a 500°C.

N.A. – No disponible.

(D) Determinación de la Gravedad Específica (S.G.) – por un Picnómetro a Gas

El polvo $CaCO_3$ (d_{50}=3.5 micrones) de Polychrom, Israel - "Girulite-8" y AR-118, un producto del invento actual, fueron evaluados en un AccPyc 1330 ex Micromeritics – USA. Los resultados se muestran en el Cuadro 15a como sigue:

CUADRO 15B – LOS RESULTADOS DEL EJEMPLO 14 (F)

Prueba #	Código de Muestra	Agente Activo	CO_2 (%)	Dosis (wt%)	L.B.D. 120°C (g/cm^3)	L.B.D.[6] 500°C (g/cm^3)
28	Natural $CaCO_3$	-	-	-	0,65	0.75
29	GCC-8[1]	-	-	-	0,65	0.56
30	GCC-8[2]	A. Decanoico	N.A.	2.0	0,64	0.56
31	PCC[3]	N.A.	N.A.	N.A.	0,71	0.55
32	PCC[4]	A. Decanoico	N.A.	2.0	0,70	0.53
33	OM-95[A]	-	-	-	0,66	0,49
34	UPCC[B]	N.A.	N.A.	N.A.	0,50	0,37
35	AR-81	A. Decanoico	100.0	0.5	0,31	0,23
36	AR-83	A. Decanoico	100.0	1	0,30	0,22
37	AR-118	A. Decanoico	100.0	2	0,25	0,18
38	AR-119	A. Decanoico	100.0	5**	0,29	0,19
39	AR-135	A. Decanoico	100.0	1	0,31	0,24
40	AR-120	A. Decanoico	100.0	2***	0,23	0,18
41	ARP-35	A. Decanoico	26.0	1.5	0,33	0,18
42	ARP-36	A. Decanoico	26.0	2.0	0,33	0,20
43	ARP-61	A. Decanoico	100.0	2.0	0,38	0,25
44	ARP-62-1	A. Decanoico	100.0	3.0	0,31	0,28
45	ARP-51	A. Laurico	26.0	1.5	0,31	0,17
46	ARP-65	A. Laurico	50.0	1.5	0,38	0,21
47	ARP-76[5]	A.Undecilenico	50.0	1.5	0,38	0,18
48	ARP-77	A. Miristico	50.0	1.5	0,37	0,18
49	ARP-70[7]	A. Steárico	50.0	1.5	0,37	0,19
50	ARP-71	A. Isosteárico	50.0	1.5	0,69	0,53
51	ARP-72	A. Oleico	50.0	1.5	0,92	0,53
52	ARP-83	A. Palmítico	50.0	1.5	0,86	0,54

** - 5g de AR-119 fueron disueltos en una solucion de HCl al 10%. El ácido no decanoico podría ser detectado o extraído, como se espera de dichas moléculas cuando son sujetas a calentamiento duante 8 horas a 500°C.

*** - 50ppm de ácido foscórico fueron utilizados además del ácido decanoico.

[1] -"Girulite-8" polvo de CaCO3 d50=3.5 micrones) ex Polychrom – Israel.

[2] – "Girulite-8" polvo de CaCO3 (d50=3.5 micrones) ex Polychrom - Israel, que fue revestido usando el 2 wt% n-ácido decanoico.

[3] – PCC Comercial– Aragonito (SSA = 12 m^2/g); de Specialty Minerals Inc. (SMI); Opacarb® A40.

[4] – PCC Comercial– Aragonito; de Specialty Minerals Inc. (SMI); Opacarb® A40, que fue revestido utilizando el 2 wt% de ácido n-decanoico.

[5] - 50ppm of ácido fosfórico fueron utilizados además del ácido decanoico.

[6] –El espectro XRD y el SEM son presentados en la Fig. 6 y Fig. 7, respectivamente.

[7] –El espectro XRD y el SEM de ARP-70 son presentados en la Fig. 8 y Fig. 9, respectivamente.

[8] – El L.B.D. del poder calcinado fue determinado de manera similar.

[A]–Acido estearico ultrafino comercial revestido - UFT 95 GCC calcita natural (95 wt% pasa tamaño 2μ) ex Omya-Pluess-Staufer - Suiza.

[B] – Cacido esteárico ultrafino comercial (SSA = 19 m^2/g) revestido - Ultraflex calcita PCC ex SMI - USA.

N.A. - No Disponible.

Los resultados en los Cuadros 13 y 15b representan los productos del invento actual si ellos tienen un L.B.D. <0,50 g/cm^3. Sin embargo, estos resultados cuentan, si el SSA (BET) de las muestras específicas en la prueba son <15 m^2/g y ellas son revestidas por los agentes activos respectivos que fueron usados (a fin de minimizar las variaciones de las interacciones de superficie). Aquellas muestras que no cumplen con este requisito, tan solo pueden ser evaluadas de acuerdo al EJEMPLO 14(E).

Conclusion: el producto (y proceso) en cuestión pertenecerá al intento actual, si este pasa ya sea la prueba (es decir L.B.D. <0,50 g/cm^3) de la prueba T.B.D. (es decir T.B.D. < 0,70 g/cc^3). En caso que el producto fallare en aprobar ambas pruebas (T.B.D. & L.B.D.),sus valores S.G. (de acuerdo al EJEMPLO 14 (E)) determinará si este el producto (el proceso) de acuerdo a una incorporación del invento actual.

Se puede observar que cambios dramáticos L.B.D. ocurran cuando el producto del presente invento sean sujetos a tratamientos de alta temperatura a 300°C (ver Cuadro 14) y especialmente a 500°C (ver Cuadro 15), que se deben probablemente a colapsos térmicos de la estructura "porosa" de estas partículas.

(G) <u>Determinación de la Densidad de Peso Perforado (T.B.D.) de un producto secado a 120°C</u>

Un modelo secado (a 120°C durante doce horas) fue desaglomerado suavemente utilizando un mortero/pistadera y colado a través de un pantalla de 0,6 mm. El

Conclusión: el producto (y el proceso) en cuestión pertenecerá al invento actual, si este aprueba ya sea la prueba (es decir T.B.D. <0,70 g/cm^3) o la prueba L.B.D. (es decir L.B.D. < 0,50 g/cc^3). En caso que el producto fallase en pasar ambas pruebas (T.B.D. & L.B.D.),sus valores S.G. (de acuerdo al EJEMPLO 14 (E)) determinarán si el producto (el proceso) de una incorporación del invento actual.

(H)Determinación de la Gravedad Específica (S.G.) en los Aceites de Productos Secados en 120°C

La gravedad específica de varias partículas de carbonato de calcio, como se describen en el Ejemplo 14 (A). Los resultados indican que los valores bajos S.G. no son debido al aceite elevado que fue usado, pero es bastante común a muchos líquidos similares. En casos en que los valores S.G. son cercanos a 2,5 g/cm^3, el ácido oleico bien definido (de pureza > 97%) puede ser utilizado para resolver cualquier disputa, en cualquier caso, las instrucciones en el EJEMPLO 14(A) y el EJEMPLO 14 (E), aun prevalecerán.

Los puntos específicos del proceso – modo continuo de operación:

1.Velocidad de Rotor = 2500 rpm (Diámetro de Rotor = 8,5 cm)

2. pH = 9,5±0,2

3. Temperatura = 85°C±3

4.Indice de fluido de dióxido de carbono = 2 m^3/hr.

5.Mezcla acuosa de hidróxido de calcio (de Shfeya) -10 wt.% = ~ 50-70 L.P.H. (para mantener el valor prefijado pH).

6.Concentración de agente activo = ácido decanoico; 0 - 2 wt.% en base a $CaCO_3$.

7.Volumen de reactor=30 l. (Diámetro=8,7cm).

Los resultados son como siguen:

CUADRO 15D – LOS RESULTADOS DE EJEMPLO 14 (H):

Prueba #	Código de Muestra	Agente Activo	Dosis (wt%)	CO2 (%)	Líquido[6,7]	S.G.[7] g/cm^3 120°C
70	GCC-8[1]	-	-	-	Sylvatal 20S	2.63
71	PCC[3]	-	-	N.A.	Sylvatal 20S	2.56

REIVINDICACIONES

1. Un proceso para producir carbonato de calcio aragonito precipitado particular, que comprende una mezcla acuosa de hidróxido de calcio con un gas seleccionado del grupo que consiste de un dióxido de carbono y un gas que lo contiene, en donde los parámetros del mencionado proceso, incluyendo por lo menos un agente activo preseleccionado, modo de operación, concentraciones de operación de materias primas, temperatura de operación, velocidad de mezclador de operación y pH de operación, son tales que por lo menos uno de los siguientes criterios (a), (b) y (c) son satisfechos:

(a) la gravedad específica del producto después del secado durante 12 hr a 120°C es <2,5 g/cm^3 y la gravedad específica de este producto seco después del encendido durante 8 hr a 500°C es <2,5 g/cm^3;

(b) la aparente (suelta) densidad de peso (L.B.D.) del producto después de secado por 12 hr a 120°C es <0,50 g/cm^3;

(c) la densidad perforada del peso (T.B.D.) del producto después de secado durante 12 hr a 120°C es <0,70 g/cm^3.

2. Un proceso de acuerdo a la Reivindicación 1, **CARACTERIZADO PORQUE** por lo menos un agente activo es seleccionado del grupo consistente en ácidos carboxílicos de fórmula RCOOH, en donde R es un grupo orgánico que contiene de 7-20 de átomos de carbono, sus sales carboxilatos, sus anhídridos ácidos, sus éteres, sus hálidos ácidos y sus quetonas.

3. Un proceso de acuerdo a la Reivindicación 2, **CARACTERIZADO PORQUE** por lo menos un agente activo es seleccionado del grupo consistente en ácidos carboxílicos de fórmula $C_nH_{2n+1}COOH$, en donde n es 8-17, sus sales carboxilatos, sus anhídridos ácidos, sus ésteres, sus hálidos acilos y sus quetonas de la fórmula $C_nH_{2n+1}C=C=O$, en donde n es 7-16.

4. Un proceso de acuerdo a la Reivindicación 2, **CARACTERIZADO POR** las siguientes características:

(a) por lo menos un agente activo mencionado que es seleccionado del grupo consistente en ácido carboxílicos de fórmula $CH_3(CH_2)_n COOH$, en donde n es 7-16, sus sales carboxilatos, sus anhídridos ácidos, sus ésteres, sus hálidos acilos y sus quetonas de la fórmula $CH_3(CH_2)_n C=C=O$, en donde n es 6-15;

(b) la concentración mencionada de por lo menos un agente activo se encuentra dentro del orden entre el 0,2 wt% y 10 wt%, calculados como ácido(s) carboxílico(s) y en base al peso del carbonato de calcio;

(c) la mezcla mencionada contiene hidróxido de calcio en una concentración dentro del orden del 3 wt% a 30 wt.%;

(d) pH mencionado se encuentra dentro del orden de 8 al 11;

(e) la temperatura mencionada se encuentra en el orden entre los 60°C y la temperatura de ebullición de la mezcla de reacción;

(f) forma de operación mencionada es seleccionada de un modo continuo y semi-continuo (intermitente);

(g) velocidad mencionada periférica del mezclador (velocidad-punta) se encuentra por encima de los 5 m/s.;

(h) por lo menos un agente activo es añadido de manera seleccionada desde la introducción al reactor de carbonación y premezclando con la mezcla mencionada de hidróxido de calcio previo a la reacción con el gas mencionado.

5. Un proceso de acuerdo a la Reivindicación 4, **CARACTERIZADO** adicionalmente de por lo menos una de las siguientes características:

(a) por lo menos un agente activo mencionado sea seleccionado del grupo consistente de ácidos carboxílicos de fórmula $CH_3(CH_2)_n COOH$, en donde n es 7-12, y las sales de calcio del mismo;

(b) concentración mencionada de por lo menos un agente activo se encuentra dentro del orden entre 0,3 wt.% y 5 wt.%, calculado como ácido carboxílico(s) con base al peso del carbonato de calcio;

(c) mezcla mencionada que contiene hidróxido de calcio dentro del orden de 4 wt% a 20 wt.%;

(d) pH mencionado se encuentra dentro del rango de 9 a 10;

(e) temperatura mencionada se encuentra dentro del orden entre 80°C y la temperatura de ebullición de la combinación de la reacción;

(f) modo de operación mencionado es un modo continuo de operación.

6. Un proceso de acuerdo a la Reivindicación 5, **CARACTERIZADO POR** lo menos por una de las siguientes características, es decir:

(a) el agente activo mencionado es seleccionado del grupo que consiste en ácido nonanoico, ácido decanoico, ácido undecanoico y las sales de calcio del mismo,

(b) concentración mencionada de por lo menos un agente activo que se encuentra dentro del orden entre 0,4 wt% y 3 wt.%, calculado como ácido carboxílico y con base al peso del carbonato de calcio,

(c) la temperatura mencionada se encuentra dentro del orden entre 90°C y la temperatura de ebullición de la combinación, y

(d) la mezcla mencionada contiene hidróxido de calcio en una concentración dentro del orden entre 5 wt% a 15 wt.%.

7. Un proceso de acuerdo a la Reivindicación 6, **CARACTERIZADO** además de por lo menos una de las características siguientes, es decir:

(a) un agente activo mencionado es seleccionado del grupo consistente de ácido decanoico y las sales de calcio del mismo,

(b) concentración mencionada de por lo menos un agente activo se encuentra dentro del orden entre 0,4 wt.% y 3 wt.%. calculado como ácido carboxílico y en base al peso del carbonato de calcio.

(c) la temperatura mencionada se encuentra dentro del orden entre 90°C y la temperatura de ebullición de la combinación de la reacción, y

(d) la mezcla mencionada contiene hidróxido de calcio en una concentración dentro del orden de 5 wt% a 15 wt.%.

8. Un proceso de acuerdo a la Reivindicación 2, **CARACTERIZADO** además por las siguientes características:

(a) por lo menos un agente activo mencionado es seleccionado del grupo consistente en ácido carboxílicos de fórmula $C_nH_{2n+1}COOH$, en donde n es 8-17, sus sales carboxilatos, sus anhídridos ácidos, sus éteres, sus hálidos ácidos y sus quetonas de la fórmula $C_nH_{2n-1}C=C=O$, en donde n es 7-16;

(b) la concentración mencionada de por lo menos un agente activo se encuentra dentro del orden entre 0,2 wt% y 10 wt% calculado como ácido(s) carboxílicos y en base al peso de carbonato de calcio;

(c) la mezcla mencionada contiene hidróxido de calcio en una concentración dentro del orden de entre 3 wt% a 30 wt%;

(d) pH mencionado se encuentra dentro del orden de 8 a 11;

(e) temperatura mencionada se encuentra dentro del orden entre 60°C y la temperatura de ebullición de la combinación de la reacción;

(f) modo de operación mencionado es seleccionado de un modo de operación continuo y un semi - continuo (intermitente);

(g) velocidad mencionada periférica del mezclador (velocidad-punta) se encuentra por encima de 5 m/s;

(h) por lo menos un agente activo mencionado es añadido en una forma seleccionada de la introducción al reactor de carbonación y premezclando con mezcla de hidróxido de calcio previa a la reacción con el mencionado gas.

9. Un proceso de acuerdo a la Reivindicación 8, **CARACTERIZADO** además por lo menos una de las siguientes características, es decir:

(a) agente activo mencionado es seleccionado del grupo consistente en ácido undecilenico y las sales del calcio del mismo,

(b) la concentración mencionada de por lo menos un agente activo mencionado se encuentra dentro del orden entre 0.4 wt.% y 3 wy.%, calculado como ácido carboxílico y con base al peso del carbonato de calcio,

(c) temperatura mencionada se encuentra en el orden entre el 80°C y la temperatura de ebullición de la mezcla de la reacción,

(d) el pH mencionado se encuentra dentro del orden de 9 a 10, y

(e) la mezcla mencionada contiene hidróxido de calcio en una concentración dentro del orden del 5 wt% a 15 wt%.

10. Un proceso de acuerdo a la Reivindicación 1, **CARACTERIZADO P RQUE** el proceso es conducido como un proceso de flotación en una celda de flotación.

11. Un aragonito precipitado particular obtenido según el procedimiento de la reivindicación 1, **CARACTERIZADO PORQUE** contiene por lo menos una sal de calcio de ácidos carboxílicos seleccionados de aquellos de la formula general $C_nH_{2n+1}COOH$ y $C_nH_{2n-1}COOH$, en donde n es 8-17, en una cantidad entre 0,2 wt% y 10 wt%, calculado como ácido(s) carboxílicos y con base al peso del carbonato de calcio.

12. Un aragonito precipitado de partículas de acuerdo a la reivindicación 11, **CARACTERIZADO PORQUE** contiene por lo menos una sal de calcio de ácidos carboxílicos seleccionados de aquellos de la fórmula general: $CH_3(CH_2)_nCOOH$,

en donde n = 7-16, en una cantidad entre 0,2 wt% y 10 wt%, calculados como ácidos carboxílicos y con base al peso del carbonato de calcio.

13. Un aragonito precipitado particular, **CARACTERIZADO POR** lo menos del siguiente criterio (a), (b) y (c):

(a) tiene una gravedad específica <2,5 g/cm^3 después del secado a 120 °C, y una gravedad específica <2,5 g/cm^3 después del encendido durante 8 hr a 500°C de producto seco;

(b) tiene un L.B.D. <0,50 g/cm^3 después de secado a 120°C durante 12 hr;

(c) tiene un T.B.D. <0,70 g/cm^3, después de secado a 120°C durante 12 hr.

14. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO POR** lo menos uno de los siguientes criterios (a), (b) y (c):

(a) tiene una gravedad específica <2,3 g/cm^3 después del secado a 120 °C, y una gravedad específica <2,3 g/cm^3 después del encendido durante 8 hr a 500°C de producto seco;

(b) tiene un L.B.D. <0,45 g/cm^3 después de secado a 120°C durante 12 hr;

(c) tiene un T.B.D. <0,60 g/cm^3, después de secado a 120°C durante 12 hr.

15. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO POR** lo menos uno de los siguientes criterios (a), (b) y (c):

(a) tiene una gravedad específica <2,1 g/cm^3 después del secado a 120 °C, y una gravedad específica <2,1 g/cm^3 después del encendido durante 8 hr a 500°C de producto seco;

(b) tiene un L.B.D. <0,40 g/cm^3 después de secado a 120°C durante 12 hr;

(c) tiene un T.B.D. <0,55 g/cm^3, después de secado a 120°C durante 12 hr.

16. Un aragonito precipitado particular **CARACTERIZADO PORQUE** tiene una gravedad específica <2,3 g/cm^3 después del secado a 120 °C, y una gravedad específica <2,3 g/cm^3 después del encendido durante 8 hr a 500°C de producto seco.

17. Un aragonito precipitado particular **CARACTERIZADO PORQUE** tiene una gravedad específica <1,5 g/cm^3 después del secado a 120 °C, y una gravedad específica <2,3 g/cm^3 después del encendido durante 8 hr a 500°C de producto seco.

18. Un aragonito precipitado particular **CARACTERIZADO PORQUE** tiene una gravedad específica de <1,5 g/cm^3 después del secado a 120 °C, y una gravedad específica <2,1 g/cm^3 después del encendido durante 8 hr a 500°C de producto seco.

19. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO PORQUE** contiene por lo menos una sal de calcio de ácidos carboxílicos seleccionados de la fórmula general $C_nH_{2n+1}COOH$ y $C_nH_{2n-1}COOH$, en donde n es 8-17, en una cantidad entre 0,2 wt% y 10 wt%, calculado como ácido carboxílico(s) y con base al peso del carbonato de calcio.

20. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO PORQUE** contiene por lo menos una sal de calcio de ácidos carboxílicos seleccionados de la fórmula general $C_nH_{2n}COOH$, en donde n es 7-16, en una cantidad entre 0,2 wt% y 10 wt%, calculado como ácido carboxílico(s) y con base al peso del carbonato de calcio.

21. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO PORQUE** contiene por lo menos una sal de calcio de ácidos carboxílicos seleccionados de ácido nonaoico, ácido decanoico, ácido undecanoico, ácido tetradecanoico, ácido octadecanoico y ácido undecilenico, en una cantidad entre 0,2 wt% y 10 wt%, calculado como ácido carboxílico(s) y con base al peso del carbonato de calcio.

22. Un proceso de acuerdo a la Reivindicación 1, **CARACTERIZADO PORQUE** la gravedad específica mencionada después del secado es <2,3 g/cm^3, la

mencionada gravedad específica después del encendido es <2,3 g/cm^3, L.B.D. mencionado es <0,45 g/cm^3 y el mencionado T.B.D. es <0,60 g/cm^3.

23. Un proceso de acuerdo a la Reivindicación 1, **CARACTERIZADO PORQUE** la gravedad específica mencionada después del secado es <2,1 g/cm^3, la mencionada gravedad específica después del encendido es <2,1 g/cm^3, L.B.D. mencionado es <0,40 g/cm^3 y el mencionado T.B.D. es <0,55 g/cm^3

24. Un aragonito precipitado particular sustancialmente puro de acuerdo a la Reivindicación 11, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) es por lo menos del 95%.

25. Un aragonito precipitado particular de acuerdo a la Reivindicación 11, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) al 90%.

26. Un aragonito precipitado particular de acuerdo a la Reivindicación 11, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) < 90%.

27. Un aragonito precipitado particular de acuerdo a la Reivindicación 11, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) > 75%.

28. Un aragonito precipitado particular de acuerdo a la Reivindicación 11, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) > 50%.

29. Un aragonito precipitado particular sustancialmente puro de acuerdo a la Reivindicación 13, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) de por lo menos el 95%.

30. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) de por lo menos 90%.

31. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) < 90%.

32. Un aragonito precipitado particular de acuerdo a la Reivindicación 13, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) > 75%.

33. Un aragonito precipitado particular de acuerdo a la reivindicación 13, **CARACTERIZADO PORQUE** es de pureza cristalográfica (aragonito/(aragonito + calcita)) > 50%.

34. Un proceso para producir carbonato de calcio precipitado particular, **CARACTERIZADO PORQUE** comprende la reacción de una mezcla acuosa de hidróxido de calcio con un gas seleccionado del grupo que consiste en dióxido de carbono y gas que lo contenga, en donde los parámetros del mencionado proceso, incluyendo por lo menos un agente activo preseleccionado, modo de operación, concentraciones de operación de materias primas, temperatura de operación, velocidad de operación de mezclador pH de operación, en donde por lo menos un agente activo es seleccionado del grupo consistente en ácidos nonanoico, ácido decanoico, ácido tetradecanoico, ácido octadecanoico y ácido undecilenico, sus sales carboxilatos, sus ácidos anhídridos, sus ésteres, sus hálidos acilos y sus quetonas.

35. Un proceso de acuerdo a la Reivindicación 34, **CARACTERIZADO PORQUE** además comprende:

(a) concentración mencionada de por lo menos un agente activo dentro del orden entre 0,2 wt% y 10 wt% calculado como ácidos carboxílicos en base al peso del carbonato de calcio;

(b) mezcla mencionada que contiene hidróxido de calcio dentro del orden del 3 wt% al 30 wt%;

(d) el mencionado pH se encuentra dentro del orden de 8 a 11;

(e) la temperatura mencionada en el orden entre 60°C y la temperatura de ebullición de la combinación de la reacción;

(f) el mencionado modo de operación es seleccionado de un proceso continuo y semi-continuo (intermitente).

(g) velocidad periférica del mezclador mencionada (velocidad-punta) por encima del los 5 m/s;

(h) por lo menos un agente activo mencionado se añade en una forma seleccionada desde la introducción al reactor de carbonación y premezclando con mezcla de hidróxido de calcio previo a la reacción del gas mencionado.

36. Un proceso de acuerdo a la Reivindicación 35, **CARACTERIZADO PORQUE** además por lo menos de una de las siguientes características:

(a) por lo menos un agente activo mencionado es seleccionado del grupo que consiste en ácido nonanoico, ácido decanoico, ácido undecanoico, ácido dodecanoico, ácido tetradecanoico, ácido ocatadecanoico, y ácido undecilenico, y las sales de calcio de las mismas;

(b) la concentración mencionada de por lo menos un agente activo se encuentra dentro del orden entre 0,3 wt% y 5 wt%, calculada como ácidos carboxílicos y en base al peso del carbonato de calcio;

(c) mezcla mencionada de hidróxido de calcio en una concentración dentro del orden de 4 wt% a 20 wt%;

(d) pH mencionado se encuentra dentro del orden de 9 a 10;

(e) la temperatura mencionada se encuentra en el orden entre 80°C y la temperatura de ebullición de la combinación de la reacción;

(f) el modo mencionado de operación es un proceso continuo de operación.

37. Un proceso de acuerdo a la Reivindicación 35, **CARACTERIZADO PORQUE** además por lo menos una de las siguientes características, es decir:

(a) el agente activo mencionado es seleccionado del grupo consistente de ácido nonanoico, ácido decanoico, ácido undecanoico, ácido undecilenico y las sales de calcio del mismo,

(b) la concentración mencionada de por lo menos un agente activo se encuentra dentro del orden entre 0.4 wt% y 3 wt%, calculado como ácido carboxílico y con base al peso del carbonato de calcio,

(c) la mencionada temperatura se encuentra en el orden entre el 90°C y la temperatura de ebullición de la combinación de la reacción,

(d) la mezcla mencionada contiene hidróxido de calcio en una concentración dentro del orden del 5 wt% a 15 wt%.

38. Un proceso de acuerdo a la Reivindicación 37, **CARACTERIZADO PORQUE** además por lo menos por una de las siguientes características, es decir:

(a) agente activo mencionado es seleccionado del grupo que consiste en ácido decanoico, ácido undecilenico y las sales de calcio del mismo,

(b) la mencionada concentración de por lo menos un agente activo se encuentra dentro del orden entre 0,4 wt% y 3 wt%, calculado como ácido carboxílico y con base al peso del carbonato de calcio,

(c) la mencionada temperatura se encuentra dentro del orden entre 90°C y la temperatura de ebullición de la combinación de reacción,

(d) la mezcla mencionada contiene hidróxido de calcio en una concentración dentro del orden del 5wt% a 15 wt%.

39. Un proceso de acuerdo a la Reivindicación 34, **CARACTERIZADO PORQUE** es conducido como un proceso de flotación en una celda de flotación.

40. Un aragonito precipitado particular sustancialmente puro de acuerdo a la Reivindicación 34, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) de por lo menos 95%.

41. Un aragonito precipitado particular de acuerdo a la Reivindicación 34, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) por lo menos 90%.

42 Un aragonito precipitado particular de acuerdo a la Reivindicación 34, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) >75%.

43. Un aragonito precipitado particular de acuerdo a la Reivindicación 34, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) >50%.

44. Un aragonito precipitado particular de acuerdo a la Reivindicación 34, **CARACTERIZADO PORQUE** la pureza cristalográfica (aragonito/(aragonito + calcita)) > 40%.

45. Una composición de revestimiento **CARACTERIZADA PORQUE** comprende un aragonito particular precipitado tal como se define en cualquiera de las Reivindicaciones 11 al 21, 24 al 33 y 40 a 44.

46. Una composición de revestimiento de acuerdo a la Reivindicación 45, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

47. Una composición de revestimiento de acuerdo a la reivindicación 45, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular en dispersión acuosa.

48. Una composición de papel **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se define en cualquiera de las Reivindicaciones de 11 al 21, 24 al 33 y 40 a 44.

49. Una composición de papel de acuerdo a la Reivindicación 48, **CARACTERIZADA PORQUE** comprende sustancialmente aragonito precipitado particular seco.

50. Un aragonito precipitado particular de acuerdo a la Reivindicación 40, **CARACTERIZADO PORQUE** comprende aragonito precipitado particular en dispersión acuosa.

51. Una composición plástica **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se define en cualquiera de las Reivindicaciones 11 al 21, 24 al 33 y 40 a 44.

52. Una composición plástica de acuerdo a la reivindicación 51, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

53. Una composición de caucho **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular como se define en cualquier reivindicación de 11 a 21, 24 a 33 y 40 a 44.

54. Una composición de caucho de acuerdo a la Reivindicación 53, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

55. Una composición absorbente **CARACTERIZADA PORQUE** comprenden un aragonito precipitado particular tal como se define en cualquiera de las Reivindicaciones de 11 a 21, 24 a 33 y 40 a 44.

56. Una composición absorbente de acuerdo a la Reivindicación 55, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

57. Una composición de detergente en polvo **CARACTERIZADA PORQUE** comprende aragonito precipitado particular tal como se define en cualquier de las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

58. Una composición de detergente en polvo de acuerdo a la Reivindicación 57, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

59. Una composición farmacéutica **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se define en cualquiera de las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

60. Una composición farmacéutica de acuerdo a la Reivindicación 59, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

61. Una composición farmacéutica de acuerdo a la Reivindicación 59, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular en dispersión acuosa.

62. Una composición agroquímica **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se define en cualquiera de las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

63. Una composición agroquímica de acuerdo a la Reivindicación 62, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

64. Una composición agroquímica de acuerdo a la Reivindicación 62, **CARACTERIZADA PORQUE** comprende aragonito precipitado en dispersión acuosa.

65. Una composición química **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se define en cualquier de las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

66. Una composición de sabor de acuerdo a la Reivindicación 65, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

67. Una composición de sabor de acuerdo a la Reivindicación 65, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular en dispersión acuosa.

68. Una composición de fragancia **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se definió en alguna de las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

69. Una fragancia de composición de acuerdo a la Reivindicación 68, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

70. Una fragancia de composición de acuerdo a la Reivindicación 68, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular en dispersión acuosa.

71. Una composición alimenticia **CARACTERIZADA PORQUE** comprende aragonito precipitado particular tal como se define en alguna de las Reivindicaciones 11a 21, 24 a 33 y 40 a 44.

72. Una composición alimenticia de acuerdo a la Reivindicación 71, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

73. Una composición alimenticia de acuerdo a la reivindicación 71, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular en dispersión acuosa.

74. Una composición alimenticia **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se define en cualquiera de las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

75. Una composición alimenticia de acuerdo a la reivindicación 74, **CARACTERIZADO PORQUE** comprende aragonito precipitado particular sustancialmente seco.

76. Una composición alimenticia de acuerdo a la reivindicación 74, **CARACTERIZADO PORQUE** comprende aragonito precipitado particular en dispersión acuosa.

77. Una composición de pantalla solar **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular como se define en las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

78. Una composición de pantalla solar de acuerdo a la Reivindicación 77, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular sustancialmente seco.

79. Una composición de pantalla solar de acuerdo a la Reivindicación 77, **CARACTERIZADA PORQUE** comprende aragonito precipitado particular en dispersión adecuada.

80. Una composición conductiva del polvo **CARACTERIZADA PORQUE** comprende un aragonito precipitado particular tal como se define en alguna de las Reivindicaciones 11 a 21, 24 a 33 y 40 a 44.

81. Una composición conductiva de poder de acuerdo a la Reivindicación 80, **CARACTERIZADO PORQUE** comprende aragonito precipitado particular sustancialmente seco.

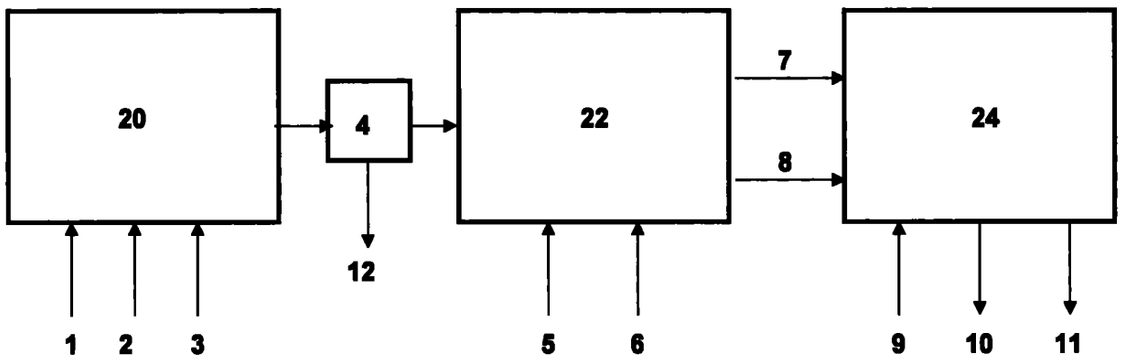

FIGURA 1

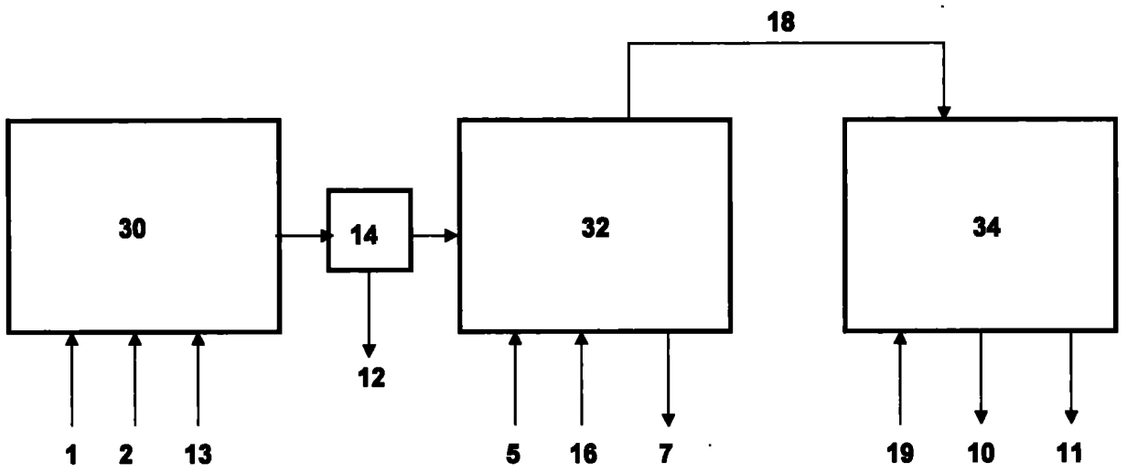

FIGURA 2

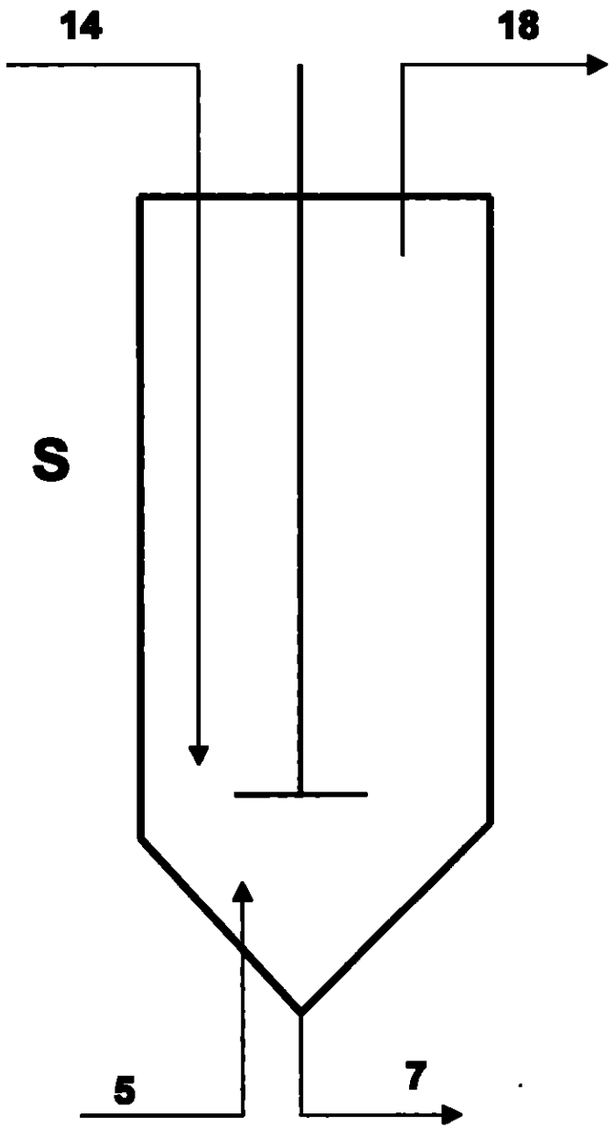

FIGURA 3

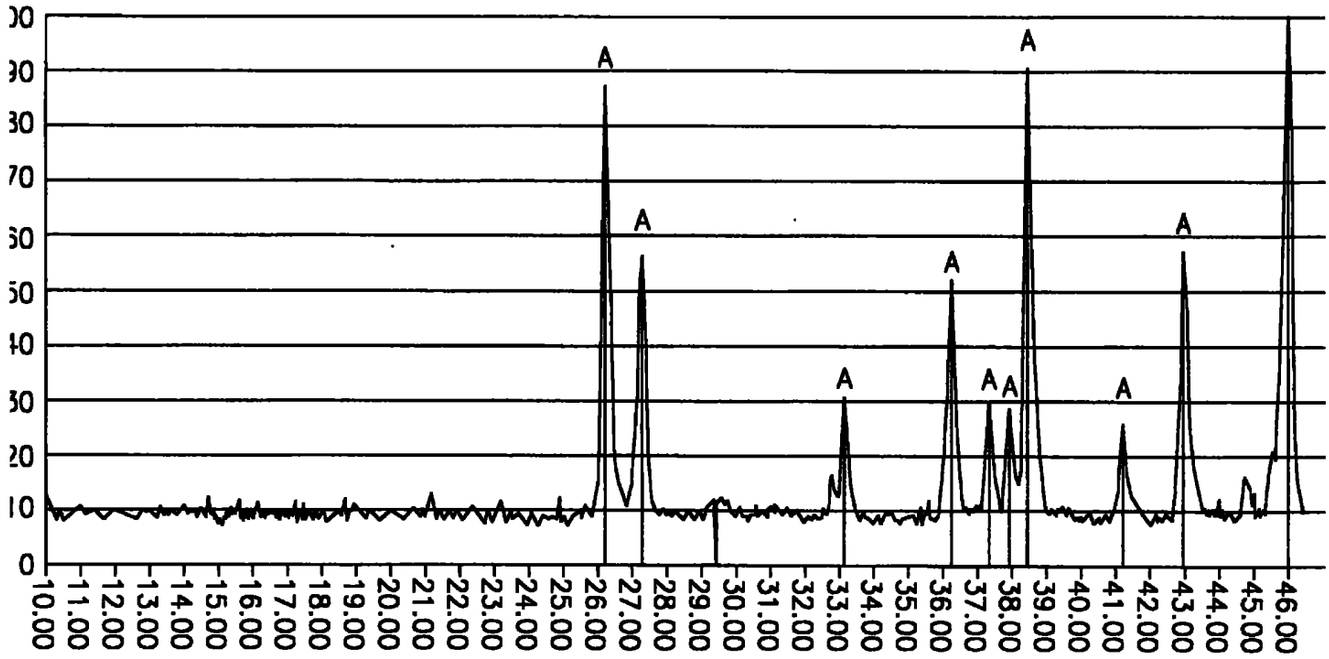
A
A
A
A
A
A
A
A
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00
26.00
27.00
28.00
29.00
30.00
31.00
32.00
33.00
34.00
35.00
36.00
37.00
38.00
39.00
40.00
41.00
42.00
43.00
44.00
45.00
46.00

FIGURE 5

197
168

PA 396265

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

April 20, 2001

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: ***09/778,920***
FILING DATE: ***February 08, 2001***

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

T. Wallace
T. WALLACE
Certifying Officer

169 26 192

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Assistant Commissioner for Patents
Washington, D.C. 20231

Atty. Dkt.: 2111-20

Date: February 8, 2001

Sir:

jc987 U.S. PTO
02/08/01

JC873 U.S. PTO
09/778920
02/08/01

Attached for filing is the patent application of:
Inventor: YANIV
Entitled: PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT
and including attachments as noted below:

- ☒ Declaration, ☒ Abstract
- 89 pages of specification and claims (including 72 numbered claims), and
- 9 sheets of accompanying drawing/s.
- ☒ Record & return the attached assignment to the undersigned.
- ☐ Priority is hereby claimed under 35 U.S.C 119 based on the following foreign applications, the entire content of which is hereby incorporated by reference in this application:

Application Number	Country	Day/Month/Year Filed

, respectively.

- ☐ Certified copy(ies) of foreign application(s) is/are attached.
- ☐ Please amend the specification by inserting before the first line –This is a of PCT application , filed , the entire content of which is hereby incorporated by reference in this application.–
- ☐ Priority is hereby claimed under 35 U.S.C 120/365 based on the following prior PCT applications designating the U.S., the entire content of which is hereby incorporated by reference in this application:

Application Number	Country	Day/Month/Year Filed

- ☐ This application is based on the following prior provisional application(s):

Application No.	Filing Date

respectively, the entire content of which is hereby incorporated by reference in this application, and priority is hereby claimed therefrom.

- ☐ Please amend the specification by inserting before the first line: --This application claims the benefit of U.S. Provisional Application No. , filed , the entire content of which is hereby incorporated by reference in this application.--
- ☒ This application is entitled to "Small entity" status. ☐ "Small entity" statement attached.
- ☐ The Examiner's attention is directed to the prior art cited in the parent application by applicant and/or Examiner for the reasons stated therein.
- ☒ Preliminary amendment to claims (attached hereto), to be entered before calculation of the fee below.
- ☐ Also attached: ☐ Information Disclosure Statement; ☐ Non-Publication Request; ☐ Other:

09/778920 02/08/01

FILING FEE IS BASED ON CLAIMS AS FILED LESS ANY HEREWITH CANCELED

Basic Filing Fee						$	710.00
Total effective claims	73	- 20 (at least 20) =	53	x $	18.00	$	954.00
Independent claims	11	- 3 (at least 3) =	8	x $	80.00	$	640.00
If any proper multiple dependent claims now added for first time, add $270.00 (ignore improper)						$	0.00
					SUBTOTAL	$	2304.00
If "small entity," then enter half (1/2) of subtotal and subtract						-$(	1152.00)
					SECOND SUBTOTAL	$	1152.00
Assignment Recording Fee ($40.00)						$	40.00
					TOTAL FEE ENCLOSED	$	1,192.00

Any future submission requiring an extension of time is hereby stated to include a petition for such time extension.
The Commissioner is hereby authorized to charge any deficiency in the fee(s) filed, or asserted to be filed, or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our Account No. 14-1140. A duplicate copy of this sheet is attached.

1100 North Glebe Road, 8th Floor
Arlington, Virginia 22201-4714
Telephone: (703) 816-4000
Facsimile: (703) 816-4100
LSN:lmy

NIXON & VANDERHYE P.C.
By Atty: Larry S. Nixon, Reg. No. 25,840

Signature: Larry S. Nixon

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

YANIV — Atty. Ref.: 2111-20

Serial No. Unknown — Group:

Filed: February 8, 2001 — Examiner:

For: PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT

* * * * * * * * * * * *

February 8, 2001

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

PRELIMINARY AMENDMENT

Prior to calculation of the filing fee and in order to place the above identified application in better condition for examination, please amend the specification and claims as follows:

IN THE SPECIFICATION

Page 1, after the title and before "FIELD AND BACKGROUND OF THE INVENTION" insert the following:

— This is a continuation-in-part of application Serial No. 09/519,749, filed March 6, 2000, now pending, the entire content of which is hereby incorporated by reference in this application. —.

IN THE CLAIMS

28. A particulate precipitated aragonite according to claim 19, which is characterized by at least one of the following features:

(i) it contains at least one calcium salt of carboxylic acids selected from those of the general formulae $C_nH_{2n+1}COOH$ and $C_nH_{2n-1}COOH$, where n is 8-17, in an amount between 0.2 and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate;

(ii) it has an XRD spectrum substantially in accordance with Figure 5 of the attached drawings.

31. A particulate precipitated aragonite according to claim 11, of crystallographic purity (aragonite/(aragonite + calcite)) at least 90%.

32. A particulate precipitated aragonite according to claim 11, of crystallographic purity (aragonite/(aragonite + calcite)) <90%.

33. A process according to claim 1, wherein said specific gravity is determined substantially as described in Example 14 (F).

34. A particulate precipitated aragonite according to claim 11, wherein said specific gravity is determined substantially as described in Example 14 (F).

35. A coating composition which comprises a particulate precipitated aragonite as defined in claim 11.

38. A paper composition which comprises a particulate precipitated aragonite as defined in claim 11.

41. A plastics composition which comprises a particulate precipitated aragonite as defined in claim 11.

43. A rubber composition which comprises a particulate precipitated aragonite as defined in claim 11.

45. An adsorbent composition which comprises a particulate precipitated aragonite as defined in claim 11.

47. A powder detergent composition which comprises a particulate precipitated aragonite as defined in claim 11.

49. A pharmaceutical composition which comprises a particulate precipitated aragonite as defined in claim 11.

52. An agrochemical composition which comprises a particulate precipitated aragonite as defined in claim 11.

55. A flavor composition which comprises a particulate precipitated aragonite as defined in claim 11.

58. A fragrance composition which comprises a particulate precipitated aragonite as defined in claim 11.

61. A food composition which comprises a particulate precipitated aragonite as defined in claim 11.

64. A feed composition which comprises a particulate precipitated aragonite as defined in claim 11.

67. A sunscreen composition which comprises a particulate precipitated aragonite as defined in claim 11.

70. A conductive powder composition which comprises a particulate precipitated aragonite as defined in claim 11.

REMARKS

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "Version with markings to show changes made."

The above amendments are made to place the claims in a more traditional format.

Respectfully submitted,
NIXON & VANDERHYE P.C.
By: Larry S. Nixon
Larry S. Nixon
Reg. No. 25,640

LSN:lmy

1100 North Glebe Road, 8th Floor
Arlington, VA 22201-4714
Telephone: (703) 816-4000
Facsimile: (703) 816-4100

VERSION WITH MARKINGS TO SHOW CHANGES MADE

28. A particulate precipitated aragonite according to [any one of claims 19 to 27] claim 19, which is characterized by at least one of the following features:

(I) it contains at least one calcium salt of carboxylic acids selected from those of the general formulae $C_nH_{2n+1}COOH$ and $C_nH_{2n-1}COOH$, where n is 8-17, in an amount between 0.2 and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate;

(II) it has an XRD spectrum substantially in accordance with Figure 5 of the attached drawings.

31. A particulate precipitated aragonite according to [any one of claims 11 to 27] claim 11, of crystallographic purity (aragonite/(aragonite + calcite)) at least 90%.

32. A particulate precipitated aragonite according to [any one of claims 11 to 27] claim 11, of crystallographic purity (aragonite/(aragonite + calcite)) <90%.

33. A process according to [any one of claims 1 to 10] claim 1, wherein said specific gravity is determined substantially as described in Example 14 (F).

34. A particulate precipitated aragonite according to [any one of claims 11 to 27] claim 11, wherein said specific gravity is determined substantially as described in Example 14 (F).

35. A coating composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

38. A paper composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

41. A plastics composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

43. A rubber composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

45. An adsorbent composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

47. A powder detergent composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

49. A pharmaceutical composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

52. An agrochemical composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

55. A flavor composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

58. A fragrance composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

61. A food composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

64. A feed composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

67. A sunscreen composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

70. A conductive powder composition which comprises a particulate precipitated aragonite as defined in [any one of claims 11 to 27] claim 11.

Our Ref.: 2111-20

U.S. PATENT APPLICATION

Inventor(s): Isaac YANIV

Invention: PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT

NIXON & VANDERHYE P.C.
ATTORNEYS AT LAW
1100 NORTH GLEBE ROAD
8TH FLOOR
ARLINGTON, VIRGINIA 22201-4714
(703) 816-4000
Facsimile (703) 816-4100

SPECIFICATION

PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT

FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to a novel form of particulate precipitated calcium carbonate, and particularly to a novel form of particulate precipitated aragonite, and to a novel process for producing it.

Various routes are known for the production of calcium carbonate, which finds use as a thickening material, as a filler, as an extender, and most of all as a pigment, in a variety of industries such as pharmaceuticals, agrochemicals, plastics, adhesives, printing, coating (paint), paper, rubber and in filtration. For such purposes, there may be used ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC). PCC in general possesses advantages over GCC, in that it is economical to produce and its precise composition, or purity, can be more strictly controlled.

The most frequently used chemical process for producing PCC is based on the carbonation of aqueous suspensions of calcium hydroxide (also known as "milk of lime" or "slaked lime") with carbon dioxide gas, or with a carbon dioxide containing gas. This process gives rise to relatively pure precipitated calcium carbonate and is a preferred process, because there are no serious problems of contamination of the product with undesired salts, and moreover it can be controlled in order to adjust the properties of the final product. Thus, the process is based essentially on four stages: firstly, calcination of raw limestone to produce calcium oxide or "quicklime" and carbon dioxide gas or a carbon dioxide containing gas; secondly, "slaking" of the quicklime with water to produce an aqueous suspension of calcium hydroxide; thirdly, carbonation of the calcium hydroxide with carbon dioxide gas or a carbon dioxide containing gas; and finally, downstream operations such as dewatering, drying, deagglomeration, grinding, surface treatment, surface coating, mixing with other minerals (e.g. titanium dioxide, talc, kaolin, GCC, PCC – including aragonite PCC) and dyeing, which allow optimization of the properties of the precipitated calcium carbonate particles in order to be adapted to their intended uses.

Calcium carbonate can be precipitated from aqueous calcium hydroxide slurries or solutions in three different crystallographic forms (polymorphs): the vaterite form which is thermodynamically unstable, the aragonite form which is metastable under normal ambient conditions of temperature and pressure, and the calcite form which is the most stable and the most abundant in nature. These forms of calcium carbonate can be prepared by carbonation of slaked lime by suitable variations of the process conditions.

The calcite form is easy to produce on industrial scales, as precipitated calcium carbonate particles. It exists in several different shapes, of which the most common are the rhombohedral shape and the scalenohedral shape.

Aragonite forms crystals having a length/width ratio (hereinafter - "aspect ratio") in the range between >1:1 and 100:1 of which a typical aspect ratio is 10, in which case the aragonite forms long, thin needles. Therefore, aragonite having a high aspect ratio may be denoted hereinafter - "acicular aragonite" or "needle-shaped aragonite". The production of aragonite is a slow process and is very difficult to control on an industrial scale.

PCC particles are used as thickening materials, fillers, extenders and, most of all, as inexpensive pigments. The latter use implies that a particularly desirable property of this material is its light scattering characteristics, in order to be able to impart opacity and brightness to the products containing it. Such characteristics are optimized, when the pigment particles are very effectively dispersed and are apart by an average distance in the range between 0.2μm and 0.4μm in their final products, and their size distribution is in the range between 0.2μm and 0.4μm, namely, in the range of half a wavelength of the visible light. That means that either the production of the PCC should be adjusted to produce small particles in order to avoid expensive downstream particle size reduction operations and to cope with the expensive problems of dewatering and drying the product, or, alternatively, the process should be adjusted to produce large particles, and subsequently effect the downstream dewatering and grinding operations. In both cases, the production costs of precipitated calcium carbonate of pigment grades may be doubled or tripled just because of these unavoidable downstream steps.

High light scattering pigments currently available to the above-mentioned industries include titanium dioxide particles, which are very effective to scatter the light due to their relatively high refractive index (2.76; for the rutile form) and their meticulously controlled particle size distribution of which median is in the range between 0.2μm and 0.4μm. However, this product is of a high specific gravity (~4.0g/cm^3), of a high surface area due to its small particles, and most of all, is quite expensive. Fine kaolin particles are also being used as pigments, but this product, which has a much lower refractive index (1.56), is of limited whiteness and is still relatively expensive. Particulate calcium carbonate is the ideal least expensive pigment and could replace much more of the titanium dioxide and kaolin pigments in their respective present applications, if it could be prepared in a form having improved light scattering properties.

Calcium carbonate pigments are produced in part by grinding coarse natural rocks and in part by precipitation processes. Of the precipitated calcium carbonate particles, a

particulate precipitated aragonite is considered to be the most effective light scattering calcium carbonate pigment, of which refractive indices are 1.530, 1.681 and 1.685, depending on its crystallographic surfaces, its specific gravity is above 2.5g/cm^3, and is the most suitable for same applications. However, its production rate is characteristically very slow and its production conditions are very difficult to control, industrially.

While the majority of references, cited hereinafter, relate to the technology for producing a particulate precipitated aragonite, some of the references are included in order to better present the state of the art for the production of PCC more generally, including the downstream operations, which may be common to all these processes and also to the present invention.

1. U.S. Patent No. 2,081,112 (N. Statham et al.) describes a process for producing precipitated calcium carbonate by carbonating milk of lime with carbon dioxide containing gas, where the temperature in the gas absorber is maintained at 50-60°C, preferably around 55°C. It is recognized that the more violent the agitation in the gas absorber, the finer will be the product; the aim being to create a fine mist of calcium hydroxide slurry.

2. U.S. Patent No. 2,964,382 (G. E. Hall, Jr.) describes production of precipitated calcium carbonate by various chemical routes, in which calcium ions are contacted with carbonate ions in a precipitation zone, the process including also carbonation of milk of lime with carbon dioxide gas. A high shear stator/rotor agitator is used to provide turbulence by rotating at a peripheral speed of at least 1160 feet per minute (589 cm per second) in the precipitation zone. Also, this patent teaches that it is desirable to operate the process at pH values of at least 8.5 and that at temperatures above 60°C, needle-shaped precipitated aragonite particles are formed, which however produce an adverse flow property effect.

3. U.S. Patent No. 3,320,026 (W. F. Waldeck) describes the production of various forms of precipitated calcium carbonate.

4. GB Patent No. 941,900 (assigned to Kaiser Aluminium & Chemical corporation) describes the production of precipitated aragonite particles, for use as a filter aid, by reacting continuously sodium carbonate solution and aqueous calcium hydroxide slurry at temperatures higher than 60°C in a multistage system. The product and the solution are withdrawn at the third stage from the bottom of the reactor, the product is then separated from the solution and part of the crystals are recycled to the various stages of the process as seeds for further precipitation of the precipitated aragonite particles.

5. U.S. Patent No. 3,669,620 (M. C. Bennett et al.) describes a continuous process for the production of a particulate precipitated aragonite by carbonating aqueous calcium

hydroxide slurry in sucrose solutions. However, due to the cost of the sucrose, the solution had to be recycled and detrimental materials had to be removed by anion exchange resin. The preferred temperature range was between 60°C and 90°C; the pH values were in the range between 7 and 9; and the concentration of the calcium hydroxide was quite low - in the range between one-half and one-twentieth molar.

6. U.S. Patent No. 4,018,877 (R. D. A. Woode) describes carbonation of calcium hydroxide slurry, wherein a complexing agent for Ca^{++} is added to the suspension in the gas absorber, after the calcium carbonate primary nucleation stage and before completion of the carbonation step, the complexing agent being e.g. citric acid, ethylenediamine tetraacetic acid (EDTA), aminotriacetic acid, aminodiacetic acid or a hydroxy polycarboxylic acid. Optionally, long-chain fatty acids or their salts can be added, preferably, after the final carbonation stage.

7. U.S. Patent No. 4,157,379 (J. Arika et al.) describes the production of a chain-structured precipitated calcium carbonate by the carbonation of calcium hydroxide suspended in water in the presence of chelating agents, such as aliphatic carboxylic acids, and water-soluble metal salts.

8. U.S. Patent No. 4,244,933 (H. Shibazaki et al.) describes a multi-stage production process for producing a particulate precipitated aragonite, using aqueous calcium hydroxide slurry and carbon dioxide gas or a carbon dioxide containing gas, in the presence of phosphoric acids and water-soluble salts thereof.

9. U.S. Patent No. 4,420,341(T. H. Ferrigno) describes inorganic fillers (including calcium carbonate) surface modified with carboxylic acids, antioxidants and high-boiling non-reactive liquid agents.

10. JP Patent Publication No. 63260815 (H. Shibata et al.) describes the production of a particulate precipitated aragonite, by reacting carbon dioxide gas with an aqueous calcium hydroxide slurry in presence of phosphoric acid, a phosphoric acid compound, a barium compound and a strontium compound.

11. JP Patent No. 1261225 (H. Shibata et al.) describes reacting carbon dioxide gas with an aqueous calcium hydroxide slurry, in order to produce a particulate precipitated aragonite, which is stated to have improved properties compared with particulate precipitated calcite.

12. U.S. Patent No. 4,824,654 (Y. Ota et al.) describes a process for producing precipitated needle-shaped (5-100 μm) particulate precipitated aragonite, in which a relatively dilute aqueous calcium hydroxide solution (0.04-0.17 wt.%) and carbon dioxide

gas or a carbon dioxide-containing gas are reacted together at a temperature of not less than 60°C, in a continuous or semi-continuous (intermittent) manner.

13. U.S. Patent No. 5,043,017 (J. D. Passaratti) describes a process for producing acid-stabilized precipitated calcium carbonate particles.

14. U.S. Patent No. 5,164,172 (H. Katayama et al.) describes a process for producing a particulate precipitated aragonite, in which a mixture of aqueous calcium hydroxide slurry, aragonite calcium carbonate particles and a water-soluble phosphoric acid compound are premixed prior to the addition of carbon dioxide gas.

15. U.S. Patent No. 5,342,600 (I. S. Bleakley et al.) describe a process of producing particulate precipitated calcium carbonate, in which aqueous calcium hydroxide slurries of varying concentrations are reacted with carbon dioxide-containing gas under a controlled mixing speed. It is recommended therein to prepare the aqueous calcium hydroxide suspension under high shear mixing and subsequently to lower the energy and shear agitation in the reaction mixture in which the precipitated calcium carbonate particles are formed.

16. U.S. Patent No. 5,376,343 (P. M. Fouche) describes a process for producing various forms of particulate PCC. In the case of aragonite, a mixture of quite dilute aqueous calcium hydroxide solution and a water-soluble source of specific anions (e.g. ammonium nitrate) are premixed prior to addition of CO_2 gas.

17. U.S. Patent No. 5,380,361 (R. A. Gill) describes *inter alia* calcium carbonate particles coated with C12-C22 fatty acids salts.

18. U.S. Patent No. 5,593,489 (K-T. Wu) describes a process for producing acid-resistant calcium carbonate particles for making neutral to weakly acid paper.

19. U.S. Patent No. 5,833,747 (I. S. Bleakley et al.) describes a process for producing a particulate precipitated aragonite, in which an aqueous calcium hydroxide slurry (148g $Ca(OH)_2$ per liter of suspension) is reacted with carbon dioxide gas at an exceptionally slow rate of 0.0026 moles per minute per mole of $Ca(OH)_2$ in a batch operation.

20. WO 9852870 (B. Jackson et al.) describes a multi-stage commercial process for producing a particulate precipitated aragonite, using coarse-grained precipitated aragonite particles as a seeding material. Though the process is claimed to be industrially applicable, it is quite slow and thus of very limited economical value.

21. U.S. Patent No. 5,846,500 (J. W. Bunger et al.) describes a process for producing a particulate precipitated aragonite, in which an aqueous calcium hydroxide solution is reacted with CO_2 gas in a plug-flow reaction system.

22. U.S. Patent No. 5,846,382 (A. von Raven) describes a process for producing inorganic fillers and pigments, including particulate calcium carbonate, of improved whiteness, brightness and chromaticity.

23. U.S. Patent No. 5,861,209 (W. J. Haskins et al.) describes a process for producing a particulate precipitated aragonite, for printing, in which an aqueous calcium hydroxide slurry is first mixed with precipitated aragonite particles for seeding and then it is reacted quite slowly with carbon dioxide gas in a batch operation. After dewatering the product to a cake containing about 70% solids, it is mixed with a typical dispersant, e.g. sodium polyacrylate, and it is further dispersed. This patent discloses the use of mixtures of a particulate precipitated aragonite, with TiO_2 and other inorganic fillers, pigments and flame retardants.

24. U.S. Patent No. 5,939,036 (A. L. Porter et al.) describes a process for producing a particulate precipitated aragonite, in which aqueous mixtures of organic compounds and acids (e.g. ethanolamine and HCl) are used to dissolve impure CaO and to form a calcium hydroxide mixture, which is then reacted with carbon dioxide gas to yield various forms of PCC, depending on the temperature. Controlling the temperature of the carbonation at about 95°C leads to aragonite.

25. U.S. Patent No. 6,022,517 and U.S. Patent No. 6,071,336 (G. H. Fairchild et al.) describe a process for producing mixtures of precipitated acicular calcite and acicular aragonite particles in the ratio of 75:25 to 25:75, by reacting carbon dioxide gas or a carbon dioxide containing gas and aqueous calcium hydroxide in the presence of a water soluble aluminum compound, by controlling the specific conductivity in a range > 4.0 and up to about 7.0, milliSiemens/cm, at a reaction temperature of from 25-60°C.

26. Pigment Handbook (Vol. I-III; Edited by T. C. Patton; John Wiley & Sons, New York (1973)) describes the properties, the production processes and various uses of aragonite calcium carbonate pigment (c.f. Vol. I; Pages 119-128), as well as those of other pigments that compete in the same market like titanium dioxide, kaolin, GCC, etc. The discussion concerning the influence of the film porosity on the hiding power or opacity of a coating film (c. f. Vol. III; Pages 203-217 and especially on Page 212) may help in understanding some aspects of the present invention.

The entire contents of the above-cited literature, including patents and publications, are incorporated herein by reference. It is apparent from the state of the art that known processes for the industrial production of substantially pure particulate precipitated aragonite (>90 parts aragonite: <10 parts calcite), by reacting aqueous calcium hydroxide

slurries with carbon dioxide gas or a carbon dioxide containing gas, exhibit serious drawbacks that affect the quality and cost of the final product, as follows:

A. Some of the processes for producing particulate precipitated aragonite are conducted in aqueous solutions of extremely low concentrations of calcium hydroxide. In some cases it is specified that clear solutions, which contain less than 1 wt.% calcium hydroxide, should be used.

B. In those processes for producing particulate precipitated aragonite, which allow use of aqueous calcium hydroxide slurries, the production rates are very slow and difficult to control.

C. To increase somewhat the rates of production in processes of A and B, the prior art recommends seeding with previously produced aragonite particles. However, this complicates the production processes, especially those operated continuously, and which are otherwise of great commercial potential.

D. Dewatering of particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, obtained according to the known art gives rise to relatively wet filter cakes of which the water content is not below 30% and which may thus require a very expensive subsequent drying step.

E. Particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, of the prior art requires extensive grinding operations to optimize its particle size distribution (PSD) in order to meet the effective PSD in the range between 0.2μm and 0.4μm, mentioned above. Moreover, the grinding operation tends to contaminate the product, due to attrition of the grinding media, unless very expensive materials of construction are used for this purpose.

F. The known particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, is of limited whiteness, mainly due to the high residual impurities in the $CaCO_3/CaO$ feedstock, which it is quite difficult to remove thoroughly, on the industrial scale. Also, the low whiteness of the product is a limiting factor in choosing the suitable sources of its raw materials ($CaCO_3/CaO$).

G. Particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, frequently requires one or more post-manufacturing treatment step(s), in order to ensure that the particle surface is hydrophobic, by coating with suitable long-chain carboxylic acids and esters and/or other materials such as silicon greases, e.g. for efficient dispersal in hydrophobic media such as rubber or plastics, and/or to ensure resistance to acidic environments for use e.g. in the paper industry and in the coating industry.

H. Efforts in the prior art to increase the effective refractive index of particulate precipitated calcium carbonate, and particularly of particulate precipitated aragonite, has not so far succeeded in making this material a serious competitor to titanium dioxide.

Accordingly, it is an object of the present invention to overcome all or most of the problems encountered in the prior art, as mentioned in paragraphs A-H, above.

It is an object of the present invention to provide particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, as stated in the preceding paragraphs, by a process which is more efficient and less expensive, than those available in the prior art.

It is yet a further object of the present invention to effect such a more efficient and less expensive process as stated in the preceding paragraph, using sources of $CaCO_3$/CaO, which are presently not suitable raw materials for use as e.g. fillers, extenders and pigments, and for other applications, in all of which uses require pigments of high optical properties and high performance, whereby production costs are lowered.

Still another object of the present invention is to provide a particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, of a superior quality as stated above, in which the produced particles are treated *in situ* with a hydrophobic agent in order to avoid an extra downstream step and to fine-tune their properties to meet the requirements of consumer products like detergents and cleaning products, especially in the powder forms, toothpastes, sunscreen lotions, pharmaceuticals, agrochemicals, rubber, plastics, coatings (especially durable paints in acidic environments), inks and paper industries (especially paper production in weakly acidic media), an effect of said *in situ* treatment being lowering of production costs.

Still another object of the present invention is to carry out the above-stated more efficient and less expensive process, in a manner which gives rise to filter cakes which are relatively dry, e.g. with no more than about 20 wt.% water, right after the dewatering stage, and thus additionally lowering production costs.

Another object of the invention is to effect the above-stated more efficient and less expensive process, in such a manner that the particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, does not require, for most applications, any downstream grinding operations, except for the regular mixing systems which are in any event usually installed in the industries mentioned above, and thus additionally lowering production costs.

Most of all, it is a particular object of the present invention to provide a particulate precipitated calcium carbonate, and particularly a particulate precipitated aragonite, of a better quality than that obtained in the prior art, and especially having a higher whiteness, a lower specific gravity and a higher effective refractive index.

Other objects of the invention will appear from the description, which follows.

SUMMARY OF THE INVENTION

It has been surprisingly found in accordance with the present invention particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite calcium carbonate, which is characterized by its high whiteness, high effective refractive index, and especially by its low specific gravity (below 2.5 g/cm^3), can be produced, and that the above-mentioned objects of the present invention can be achieved, by a process which comprises reacting an aqueous calcium hydroxide slurry with a gas selected from carbon dioxide and a gas containing it, wherein the parameters of the process, including e.g. at least one preselected active agent, modes of operation, operating concentrations of raw materials, operating temperatures, operating pH range and high shear mixing speeds, are strictly controlled such that the desired product is obtained. In a particular embodiment, flotation of the product occurs during such process.

The process of the invention for producing a particulate precipitated aragonite in accordance with the invention, is preferably further characterized by at least one, and preferably all, of the following features: (a) the active agent comprises at least one member selected from the group consisting of carboxylic acids of formula RCOOH, where the organic group R (which may be e.g. a saturated or unsaturated aliphatic group, such as a hydrocarbon group which may be substituted or unsubstituted) contains 8-20 carbon atoms, and their carboxylate salts, esters, anhydrides, acyl halides, and their ketenes (b) more specifically, the active agent comprises at least one member selected from the group consisting of carboxylic acids of formula $C_nH_{2n+1}COOH$, where n is 8-16, and their carboxylate salts, esters, anhydrides, acyl halides, and their ketenes; (c) also, the active agent comprises at least one member selected from the group consisting of carboxylic acids of formula $C_nH_{2n-1}COOH$, where n is 8-16, and their carboxylate salts, esters, anhydrides, acyl halides, and their ketenes; (d) more specifically, the active agent comprises at least one member selected from the group consisting of carboxylic acids of formula $CH_3(CH_2)_nCOOH$, where n is 7-16, and their carboxylate salts, esters, anhydrides, acyl halides, and their ketenes of formula $CH_3(CH_2)_{n-1}C=C=O$; (e) the concentration of the active agent is within the range of between 0.2 wt.% and 10 wt.%, calculated as RCOOH and based on the weight of calcium carbonate; (f) the slurry contains calcium hydroxide in a concentration within the range of from 3 to 30 wt.%, more preferably 4 to 20 wt.%; (g) the product is produced at a pH between 8 and 11, preferably between 9 and 10; (h) the process is effected at a temperature in the range between 60°C, desirably between 80°C, and the boiling temperature of the reaction mixture; (i) the process is effected either in a semi-continuous (intermittent) mode of operation, or more

preferably in a continuous manner;.(j) the process is effected under high shear mixing e.g. with a mixer comprising a rotor/stator or a rotor only, the mixer peripheral (tip) speed being preferably at least 5 m/sec. In a particular embodiment, this process is effected in a continuous mode of operation under high shear mixing with a mixer comprising a rotor/stator or a rotor only, at a temperature in the range between 90°C and the boiling temperature of the reaction mixture, the active agent - preferably present in an amount in the range between 0.2% and 10 wt.%, calculated on the weight of calcium carbonate - being selected from the carboxylic acids and their calcium salts, and the slurry contains calcium hydroxide in a concentration within the range of from 5 to 15 wt.%, the active agent being desirably premixed with the calcium hydroxide slurry prior to reaction with carbon dioxide.

The present invention also provides as a novel chemical substance - which is of course obtainable in accordance with the present process, a particulate precipitated aragonite, which has a specific gravity of <2.5 g/cm^3 (preferably <2.3 g/cm^3, more preferably <2.0 g/cm^3, even more preferably <1.5 g/cm^3) after drying at 120°C, and a specific gravity <2.5 g/cm^3 (preferably <2.3 g/cm^3, even more preferably <2.1 g/cm^3) after ignition for eight hours at 500°C. In a particular embodiment, the product has a specific gravity of <2.3 g/cm^3 after drying at 120°C, and a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500°C and in another particular embodiment, the product has a specific gravity of <2.1 g/cm^3 after drying at 120°C, and a specific gravity <2.1 g/cm^3 after ignition for eight hours at 500°C.

A typical such product may be further characterized by at least one of the following features: it contains said carboxylic acid calcium salt(s) in an amount between 0.2 and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate; it has a specific gravity <2.2 g/cm^3, preferably <2.0 g/cm^3, more preferably <1.8 g/cm^3, and even more preferably <1.5 g/cm^3; a product previously dried at 120°C for 12 hours has a loss on drying at 300°C for 8 hours of about <10% wt.%, based on the weight of calcium carbonate; a product previously dried at 120°C for 12 hours has a loss on ignition at 500°C for 8 hours of about <10% wt.%, based on the weight of calcium carbonate; after drying at 120°C for 12 hours, and/or drying for 8 hours at 300°C, and/or firing for 8 hours at 500°C, it still has a specific gravity < 2.5 g/cm^3; after drying at 120°C for 12 hours, and/or drying for 8 hours at 300°C, and/or firing for 8 hours at 500°C, it has also a preferable typical loose bulk density well below 0.5 g/cm^3.

In another aspect, the present invention provides a particulate precipitated aragonite which contains at least one calcium salt of carboxylic acids selected from those of the general formula: $C_nH_{2n+1}COOH$, where n = 8-17, in an amount between 0.2 and 10 wt.%, calculated as $C_nH_{2n+1}COOH$ and based on the weight of calcium carbonate, and which has

(A) a specific gravity <2.5 g/cm^3 after drying for 12 hours at 120^{o}C, and/or (B) a specific gravity <2.5 g/cm^3 after ignition for eight hours at 500^{o}C of the product dried, preferably, in (A).

In still another aspect, the present invention provides a particulate precipitated aragonite which contains at least one calcium salt of carboxylic acids selected from those of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7-16, in an amount between 0.2 and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate, and which has (A) a specific gravity <2.5 g/cm^3 after drying for 12 hours at 120^{o}C, and/or (B) a specific gravity <2.5 g/cm^3 after ignition for eight hours at 500^{o}C of the product dried, preferably, in (A).

In still another aspect, the present invention provides a particulate precipitated aragonite which contains at least one calcium salt of carboxylic acids selected from nonanoic acid, decanoic acid, undecanoic acid and undecylenic acid in an amount between 0.2 and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate, and which has (A) a specific gravity <2.5 g/cm^3 after drying for 12 hours at 120^{o}C, and/or (B) a specific gravity <2.5 g/cm^3 after ignition for eight hours at 500^{o}C of the product dried, preferably, in (A).

The product of the present invention can be used as a builder, an anticaking material, an encapsulant, an adsorbent, a thickening material, a sunscreen, a filler, an extender and particularly as a pigment for the detergent, pharmaceuticals, agrochemicals, plastics, adhesives, printing, coating (paint), paper, rubber, filtration, toiletries and many other industries. Thus, in accordance with further aspects of the present invention, there are provided a coating composition, a paper composition, a plastics composition, a rubber composition, an adsorbent composition, a powder detergent composition, a pharmaceutical composition, an agrochemical composition, a flavor composition, a fragrance composition, a food composition, a feed composition, and a sunscreen composition, each of which comprises a particulate precipitated aragonite in accordance with the invention. For this purpose, such compositions may comprise, for example, substantially dry particulate precipitated aragonite, or particulate precipitated aragonite in aqueous dispersion.

The PCC of the present invention can be used in most of the (consumer) products that the prior art particulate calcium carbonate is being used (and quite probably in all of them). However, the PCC of the present invention will manifest its advantages and unique properties when these (consumer) products are to be produced and/or be used under conditions that exploit its porous nature as an adsorbent for liquids (e. g. in powders or

detergent powders, in pharmaceuticals, in agrochemicals and in various household products like food and feed formulations. Also, as an encapsulating agent for flavors and fragrances, pharmaceuticals and agrochemicals), and/or an anticaking agent (e. g. in powders or detergent powders, in pharmaceuticals, agrochemicals, food, and feed formulations), as a "fight" component to reduce the bulk density of products (e. g. when it is used as a filler and/or a builder in powders or detergent powders), as a thickening material (e. g. in glues, sealants, adhesives, coatings (paints), and in paper), as filler, as an extender and, particularly, as a pigment (e. g. in sunscreen formulations, plastics, adhesives, printing (inks), coatings (paints), paper (especially formulations for coating paper, and particularly for high gloss paper products), rubber, filtration, and many others).

BRIEF DESCRIPTION F THE DRAWINGS

Figure 1 shows a schematic flow sheet for production of particulate precipitated calcium carbonate according to the prior art.

Figure 2 shows a schematic flow sheet for production of a particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 3 shows in schematic vertical section, a reactor/flotation cell for producing a particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 4 shows a SEM picture of a substantially pure particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 5 shows an XRD spectrum of a substantially pure particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 6 shows a SEM picture of, ARP-76, a substantially pure particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 7 shows an XRD spectrum of, ARP-76, a substantially pure particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 8 shows a SEM picture of, ARP-70, a mixture of ~50% particulate precipitated aragonite and ~50% particulate precipitated calcite, in accordance with an embodiment of the present invention.

Figure 9 shows an XRD spectrum of, ARP-70, a mixture of ~50% particulate precipitated aragonite and ~50% particulate precipitated calcite, in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the process of the present invention, a slurry of calcium hydroxide in water and carbon dioxide gas or a carbon dioxide containing gas is reacted together in the presence of the active agent under stringent process conditions, to generate a particulate precipitated aragonite having unique properties.

The product of the present invention is characterized by its low production cost and by its unique physical properties (high whiteness, high effective refractive index and low specific gravity (<2.5g/cm3)) and by its excellent chemical properties (hydrophobicity and resistance to weak acids), which make it particularly suitable as an adsorbent for liquids, an anticaking material, a thickening material, a builder, a filler, an extender and most of all as a pigment for the printing, coating (paint), paper, rubber, plastics, filtration, adhesives,

sealants, pharmaceuticals, agrochemicals, food, feed, detergents and many other industries.

As stated above, Fig. 1 shows a flow sheet for production of particulate precipitated calcium carbonate according to the prior art. By contrast, in order to define the most suitable conditions to operate the carbonation stage of the present invention, a detailed description of parameters for the present process is given below. These also include some details of how to operate the upstream and downstream stages of the carbonation stage, as these may affect the final outcome (c. f. Figs. 2 and 3).

In Figure 1, which is a schematic representation of a prior art procedure for making a precipitated calcium carbonate, quicklime (CaO) and water, which react together giving slaked lime, are fed to reactor 20 via respective conduits 1 and 2, and optional additives such as aragonite calcium carbonate particles for seeding, phosphoric acids and salts, aluminum salts, oxides and hydroxide (other than $CaO/Ca(OH)_2$), chelating agents, dispersants, and surface active agents, may also be added at this stage via conduit 3. The initial product "milk of lime" (calcium hydroxide) is fed via filter or hydrocyclone 4 (large solid particles being removed at 12) into carbonator 22, to which there is also fed gaseous carbon dioxide (or a gas containing it) via conduit 5 and the aforementioned optional additives via conduit 6. The reaction product including any contaminants exits carbonator 22 as an underflow via conduit 7 and/or an overflow via conduit 8, to further operations (at site 24) such as dewatering, grinding and coating; for such further operations there may be added optionally via conduit 9, e.g. dispersants, surface active agents, greases, silicon greases, long-chain carboxylic acids and their salts and esters, organic and inorganic pigments, powder metals, coal, carbon black or activated carbon, and/or dyeing agents. The filtrate and water vapors exit the system via conduit(s) 10, while the final product (which may be wet or dry and optionally post-treated) exits via conduit 11.

In Figure 2, which is a schematic representation of a procedure for making a particulate precipitated aragonite in accordance with the present invention, quicklime (CaO) and water which react together giving slaked lime are fed to reactor 30 via respective conduits 1 and 2, and the present active agent (and optionally also additives such as phosphoric acids and salts, chelating agents, dispersants, and surface active agents) may be added at this stage via conduit 13. The initial product "milk of lime" (calcium hydroxide) together with active agent if added to 30 (and optional additives) is fed via filter or hydrocyclone 14 (large solid particles being removed at 12) into carbonator 32, to which there is also fed gaseous carbon dioxide (or a gas containing it) via conduit 5 and the active agent (and possibly the aforementioned optional additives) via conduit 16. It will be appreciated that the active agent may be added

either to reactor 30 or to carbonator 32, or to both. Contaminants and liquid exit carbonator 32 as an underflow via conduit 7, whereas - owing to the fact that an embodiment of the present process includes simultaneous flotation - the desired product exits as an overflow via conduit 18, to further operations (at site 34) such as dewatering, grinding and coating; for such further operations there may be added optionally via conduit 19, e.g. dispersants, surface active agents, greases, silicon greases, long-chain carboxylic acids and their salts (including if desired those within the definition of the present active agents) and esters, organic and inorganic pigments, powder metals, coal, carbon black or activated carbon, and/or dyeing agents. The filtrate and water vapors exit the system via conduit(s) 10, while the final product (which may be wet or dry and optionally post-treated) exits via conduit 11.

Slaking of quicklime

Though this operation is well known in the prior art, it is worthwhile to choose a preferred mode of operation, which is best, adapted to the process of the present invention. Thus, fresh slaked lime is preferably prepared in a continuous mode of operation, which enables operation of the downstream carbonation stage using low inventories and exploiting to its maximum the energy that is liberated in the reaction between the water and the CaO, before this precious energy is lost to the surroundings. The present invention desirably makes use of this energy to effect the step of carbonation of the aqueous calcium hydroxide slurry at relatively high temperatures, more preferably without cooling or heating, or in other words, without adding or subtracting energy, and thus utilizing only the energy liberated by the carbonation reaction together with the energy produced by a powerful mixing system. Once again, use of fresh and still warm milk of lime is preferably an important factor in the success of the carbonation stage and this is more preferably effected, as mentioned above, in a continuous mode of operation, the temperature of the slaked lime being preferably maintained at about the temperature of the carbonation stage. However, in the alternative, a batch mode of operation may also be used for process of the present invention or the CaO can be introduced directly into the carbonator, as is demonstrated in the prior art.

Mixing of quicklime

In some prior art patents it is recommended to use high shear mixers to slake the CaO with water. The process the present invention is quite tolerant to the kind of mixing, as long as the slaking reaction is complete and the maximum energy is liberated. Mixers that comprise rotor/stator mixing systems and mixers that comprise rotors only are suitable.

Purification of slaked lime prior to carbonation

There are numerous methods of purifying slaked lime before its utilization in the carbonation stage. Filtration by filters to remove large insoluble particles and/or separation of these particles by hydrocyclones are two efficient methods for this purpose. Usually, particles of greater diameter than 40 μm (up to 70 μm) are removed prior to the carbonation stage and the coarse particles can then be discarded or used in the construction industry, for example. The fine slurry is then ready for carbonation in the subsequent downstream stage. Naturally, feeding CaO directly into the carbonator, as mentioned above, does not allow to make use of such purification methods.

Sources of $CaCO_3$/CaO:

Many sources of $CaCO_3$/CaO are too contaminated to be used to produce, by known methods, a particulate precipitated aragonite for the printing, (inks), coating (paint), paper, rubber, plastics, filtration, adhesives and sealants, pharmaceuticals, household and personal care and other industries, and their main use is, as very inexpensive materials, in the construction industry. On the other hand, the present invention may allow utilizing many of these "impure" $CaCO_3$/CaO sources and turning them into a particulate precipitated aragonite, of filler, extender and pigment grades. The present invention, as is manifested in the carbonation stage, is superior over any state of the art technology in salvaging $CaCO_3$ mines and turning them to profitable use, without changing greatly the state of the art methods for preparing the slaked lime.

Use of Additives

The state of the art technology for slaking quicklime includes adding a variety of additives into the milk of lime prior to the carbonation stage. According to the present invention, one of the preferred modes of operation is to add the active agent into the milk of lime prior to the carbonation reaction. Those skilled in the art of producing precipitated calcium carbonate must carefully check that the other additives, if any are present in the milk of lime, do not interfere with the ability of the active agent to enhance formation of the particulate precipitated aragonite and to cause its flotation in the carbonation reactor. For instance, the use of 1 wt.% (based on the calcium carbonate) of phthalic acid or trimelitic acid with about 1 wt.% (based on the calcium carbonate) one of the most potent active agents of the present invention, n-decanoic acid, cause the formation of mostly the particulate calcite polymorph in the carbonation stage, under the specific conditions that are described in the experimental section. Instead of obtaining mostly the aragonite

polymorph. In other cases, the additives may cause the formation of mixtures of various concentrations of particulate precipitated calcite and aragonite, instead of quite pure particulate precipitated aragonite calcium carbonate.

The Reaction/Carbonation Stage

This operation is well known in the prior art. However, as this stage is the essence of the present invention, it is worthwhile to choose the mode of operation that suits it best. For example, although the use of aragonite particles for seeding is a recommended procedure in the prior art, it seems at the present time that this practice is unlikely to have any particular utility in the process of the present invention, since use of the active agent enables all desired objectives to be achieved.

As the most important functions of the active agent in the present invention are to catalyze the production of particulate precipitated aragonite, of improved physical and chemical properties and to cause its flotation in the carbonation reactor, all necessary measures should be taken in order to maximize these functions.

The Nature of the Active Agent and its Origin

While the scope of the present invention is not to be regarded as limited by any theory, nevertheless, it may be likely that the calcium salts of the carboxylic acids of the general formula RCOOH (of which more specific chemical structures have been mentioned already in greater details hereinbefore) operate in practice as the functioning active agent in the present process. It should not be ruled out, however, that for example, other derivatives of such acids within the scope of the invention may participate in similar activity.

The above-mentioned calcium salts of the relevant acids may be used as raw materials in the present invention. However, other compounds, which undergo chemical transformations to form the active agent under the process conditions, also serve this purpose as raw materials in the production of the desired particulate precipitated aragonite.

In a particular embodiment of the invention, which will serve here as an example, the active agent is selected from carboxylic acids of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7-16, and including mixtures thereof. All these acids can be quite easily introduced into any of the production facilities. Pumping of these acids when their temperature is held above their melting points (e.g. >60°C) seems to be a very useful method to deliver the acids into the suitable production units. Under such conditions, these

thermally stable acids are immediately converted into their respective calcium salts when they are mixed with the hot aqueous calcium hydroxide slurry or with the hot carbonation mixture at pH>7. As water is the only by-product of the reaction between the calcium hydroxide and the respective carboxylic acids, the use of these acids, as raw materials in the process of the present invention, seems to have no harmful side effect.

The respective acid anhydrides of the general formula: $(CH_3(CH_2)_nCO)_2O$, including mixtures thereof, where n = 7-16, are as good a source for the active agent, as the corresponding acids. However, the anhydrides are much less safe to handle and they are much more expensive than the respective acids.

The carboxylate salts of the acids of the general formula: $CH_3(CH_2)_nCOOH$, including mixtures thereof, where n = 7-16, can serve as raw materials in the process of the present invention, e.g. where the cations are selected from Na^+, K^+, NH_4^+, Li^+, Mg^{++} and especially Ca^{++}, but, generally, the use of these salts does not appear to have any advantage over the free acids. On the contrary, the salts are usually more expensive, they are not as easy to handle on an industrial scale as the respective acids and, except the Ca^{++} salts, all the other salts add cations that, so far as is presently known, are not required in the present process. The Mg^{++} salts present a special case, as they leads to the formation of hydromagnesite and thereby to a dramatic rise of the surface area of the product, to its contamination and to a large increase in the water content in the wet filter cake. Therefore, in the process of the present invention only limited concentrations of this cation are allowed, i.e. < 1 wt.%, based on the calcium hydroxide (this limitation is removed if it is desired to exploit the process of the present invention to produce hydromagnesite or mixtures of hydromagnesite and PCC of the present invention. On the contrary, then Mg^{++} can also be introduced as other Mg salts or, preferably, as $MgO/Mg(OH)_2$).

Esters of the following general formula: $CH_3(CH_2)_nCOOR'$, where n = 7-16 and R' is an esterification radical such as alkyl, e.g. CH_3, C_2H_5, C_3H_7, etc., are also suitable candidates for the active agent in the present invention. However, in order for these compounds to generate e.g. the corresponding calcium salts, they have to undergo a basic hydrolysis, which may preferably be done by premixing them in the hot and basic aqueous calcium hydroxide slurry, in which they are hydrolyzed and thus converted to the respective Ca^{++} salts. However, the use of these esters in the process of the present invention appears to be inferior to the use of the respective acids, for reasons, which will be self-evident to the skilled person.

Chemically equivalent to the other preferred active agents specifically mentioned above, are ketenes of the general formula: $CH_3(CH_2)_{n-1}C=C=O$, wherein n = 7-16, and including mixtures thereof, behave in a similar manner and entail similar drawbacks, as for the acid anhydrides, as mentioned above.

Therefore, the acids of the general formula: $CH_3(CH_2)_nCOOH$, wherein n = 7-16, including mixtures thereof, are the presently preferred source for the active agent to be used in the process of the present invention. More specifically, decanoic acid (wherein n=8) is presently one of the most potent and preferred acids, as it leads to products of the present invention of which the content of the aragonite isomorph is the highest, under comparable conditions. Lauric acid (wherein n=10), myristic acid ((wherein n=12) or even stearic acid (wherein n=16), relatively abundant and less expensive raw materials, may be preferred in some other cases, in which the maximum content of the aragonite ismorph in the product is not critical or in cases in which controlled concentrations of the calcite isomorph in the product of the present invention may even be desirable.

It seems that the process of the present invention is quite more general than it was thought originally. It was also found out that undecylenic (or 10-undecenoic) acid (CH_2=CH(CH2)$_8$COOH) is also a very potent active agent in the process of the present invention and others will, probably, be sorted out in the future, using the conditions of the novel process of the present invention and the simple and straight-forward methodology of how to determine which compound (carboxylic acid) is an active agent.

<u>The Reactor/Carbonator/Flotation Cell</u>

As already mentioned above, the carbonation stage can be conducted in any well-stirred reactor according to the prior art. However, due to the fact that the active agent is a unique material that can enhance the formation of the particulate precipitated aragonite of the present invention, in the reaction between aqueous calcium hydroxide slurries and carbon dioxide gas or a carbon dioxide containing gas, and also due to the fact that the active agent can cause this product to float, the presently preferred carbonators to be used in the process of the present invention are flotation cells.

These cells may be operated somewhat differently from the regular carbonators and the regular flotation cells, as both functions (carbonation and flotation) take place in the same production unit of the particulate precipitated aragonite, of the present invention. The exact set-up of these flotation cells can vary, as this will depend on, for example, the preferences of the skilled designer, the precise nature of the desired product, the quality

198

of the aqueous calcium hydroxide slurries, etc. For example, a flotation cell like that depicted in Fig. 3, containing stator/rotor or rotor only S, is suitable for carrying out the inventive process, and of which the main features are as follows:

A. The stream of slaked lime (14) is preferably introduced near the inner circumference of the reactor and above the stirring blades.

B. The stream (5) of carbon dioxide gas or carbon dioxide containing gas is preferably introduced through suitable spargers at a point below the stirring blades, but still not too close to the bottom of the cell, to avoid excessive mixing near the outlet stream (7) of the contaminants and liquid.

C. The wet product and the gas are preferably discharged from the top (18) of the cell. The customary skimmer for skimming the product out of the flotation cell, and hydrocyclones for efficient product/gas separation, are not shown in Fig. 3.

Mode of Operation in the Carbonation Step

Continuous reaction/carbonation of the aqueous calcium hydroxide slurry with carbon dioxide gas or a carbon dioxide containing gas is the most suitable mode of operation for the present invention, especially because of the huge potential market for the produced particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite.

Semi-continuous (intermittent) operations may also be used. However, as may be understood from the desirability of operating the process at its utmost efficiency, e.g. as a flotation operation, it is unlikely that an intermittent mode of operation can compete economically with the continuous mode of operation.

A "real" batch mode of operation, in which the milk of lime and the active agent are mixed together and carbon dioxide gas or a carbon dioxide containing gas is introduced to precipitate the desired product until the reaction mixture turns neutral (at about pH~7), appears not to be viable, probably because the active agent is not efficient in catalyzing the formation of desired product, at the high initial pH characteristic of the batch mode of operation in this case, and/or because the active agent is adsorbed onto the surface of the first formed crystals of particulate precipitated calcium carbonate, where it is then "buried" under the subsequent PCC. In such circumstances, the active agent is very quickly depleted from the reaction zone, and the process of the invention, as such, is likely to become inoperable.

Temperature of the Carbonation Step

The prior art teaches producing a particulate precipitated aragonite, at a temperature range between 60°C and the boiling temperature of the reaction mixture, at ambient pressure, and the present process is preferably conducted similarly, because lower temperatures favor the formation of calcite.

On the other hand, operating the process at a temperature as close as possible to the boiling point of the reaction mixture is presently particularly preferred, since these conditions give a product of relatively lower water content in the wet filter cake, which is a great advantage in many applications of the product.

While the present process may be operated at higher temperatures and pressures (since the active agent is stable under such conditions), this kind of operation is associated with serious technological problems that may adversely affect the whole economics of the process.

Concentration of $Ca(OH)_2$ slurry in the Carbonation Step

The prior art method for producing a particulate precipitated aragonite, may be classified into three principle modes of operation. The first mode is operated at very low concentrations of the calcium hydroxide in water, and in some cases a clear solution of <1 wt.% calcium hydroxide is used. In the second mode, there are used aqueous calcium hydroxide slurries and active agents to induce the formation of the desired particulate precipitated aragonite, albeit, at very low production rates. In the third mode, particulate precipitated aragonite is used for seeding, in order to improve production rates.

The present invention requires relatively high concentrations in the aqueous calcium hydroxide slurries and the production rates are very fast. Actually, at the range of very low concentrations of <2 wt.% (based on the calcium hydroxide) the present process may not "ignite" right away and under these circumstances no desirable "porous" product of the present invention is obtained, but rather, only precipitated calcite calcium carbonate particles, or mixtures of mainly such particles.

The present invention can use quite dense aqueous calcium hydroxide slurries of up to about 30 wt.% calcium hydroxide, but such dense slurries are very viscous and are very difficult to handle. Therefore, the preferred range of concentrations of the aqueous calcium hydroxide slurries, according to the present invention, are in the range between 4% and 20 wt.%, and more preferably between 5% and 15 wt.% calcium hydroxide. In these ranges, the viscosity of the reaction mixture permits smooth operation, while the energy maintained already in the feed of aqueous calcium hydroxide slurry (as discussed above),

plus the energy liberated by the carbonation reaction, as well as the energy liberated by the mixing system, are sufficient to maintain the desired reaction temperature without any external heating or cooling.

Concentration of Active Agent in the Carbonation Step

To simplify the calculations of how much active agent is needed in the process and how much of it may be included in the product of the present invention, we prefer to use the weights of the respective acids, since the carboxylate moieties differ from their respective acids by less than 1%. Therefore, in cases that suitable ketenes, esters, carboxylate salts, acid anhydrides and/or acyl halides are being used, the equivalent weight of the respective acid should be calculated, unless otherwise indicated. Moreover, as we are presently aware of differences among the activities of the acids of the general formula e. g. $CH_3(CH_2)_nCOOH$, wherein $n = 7\text{-}16$, including mixtures thereof, their individual contribution to the total weight of the active agent should be calculated arithmetically, namely by adding the weight of each individual acid, as if these are of the same chemical entity. This concept is important for understanding this invention and particularly the claims, unambiguously. The difference between the molecular weights of the respective acids (~±30%) is not a great problem, because a person skilled in the art will in any event check carefully what is the exact amount of the relevant carboxylic acids that is necessary to operate the process in a manner, which is not sensitive to even larger variations of the concentrations of the active agent, namely, of >±30 wt.%, based on $CaCO_3$. Moreover, when using decanoic acid as the presently preferred active agent, the present invention will not even be subject to the above-mentioned inaccuracy.

To determine the concentration range of the active agent in the present invention, it is important to be aware of the various functions of this agent in the production process and the effects that it produces in the final product.

The prior art describes many additives that assist in producing particulate precipitated aragonite, but none of these additives is comparable to the present active agent, under the selected process parameters, for the following two major reasons:

1. The active agent leads to a dramatic reduction of the specific gravity of the particulate product and allows use of the flotation method to separate the "light" particulate precipitated aragonite, from the "heavy" contaminants (containing aluminosilicates and heavy metal salts, carbonates and oxides). These "heavy" particles sink down to the bottom of the carbonator/flotation cell and are discharged from the production unit without reaching the downstream filter, and

2. The optical properties of the particulate precipitated product are altered and its effective refractive index is increased dramatically.

Thus, according to one of the preferred modes of operation, the pure product of the present invention, on the flotation embodiment, is being carried to the top of the reactor/carbonator/flotation cell, by the small bubbles that adhere to the tiny precipitated particles, and this relatively pure product is discharged from the top of the carbonator/flotation cell prior to any downstream operation. Thus, in this embodiment, the present process entails an intrinsic, built-in, extra purification operation, prior to the downstream dewatering operation, which is not so common in the prior art.

This unique property of the active agent to cause the flotation of the "light" particulate precipitated calcium carbonate, is also a reason why this embodiment of the present invention is superior over any of the prior art production technologies in exploiting highly contaminated sources of $CaCO_3/CaO$, which have hitherto been unsuitable as raw materials for production of a particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, of filler, extender and pigment quality grades. Such sources can now be utilized successfully, using this novel technology of the present invention.

Since the aqueous calcium hydroxide slurry is usually quite contaminated and the impurities are liable to affect performance of the active agent, the threshold (minimum) concentration of the active agent will vary, but is within the competence of a skilled person to determine, under any particular set of circumstances. Moreover, the threshold concentration will also vary with the kind of active carboxylic acids that will be used. In any case, it is desirable to avoid this threshold concentration at the carbonation stage, as this is a point of instability and would involve unnecessary risk to the desired objective. When considering use of a new feedstock of $CaCO_3/CaO$, laboratory experiments will reveal the minimum concentration of the active agent, which is necessary to start the production of the desirable particulate precipitated calcium carbonate, and particularly particulate precipitated aragonite, without any faults (vis-a-vis the pertinent $CaCO_3/CaO$ feedstock). This value is expected to be in most cases above 0.2 wt.%, preferably within the range 0.4% to 3 wt.%, based on the calcium carbonate.

It is very important to note that this threshold concentration, discussed above, for catalyzing the production of particulate precipitated aragonite, of the present invention (~0.2% wt.%, based on $CaCO_3$) is substantially above the threshold concentration that is required to cause the flotation of this product in aqueous solutions (~0.02% wt.%, based on $CaCO_3$) and that by operating in the concentration range merely for a "proper" flotation

process, nothing that is disclosed in the present invention really happens. Actually, the optimal physical and chemical properties of the particulate precipitated aragonite calcium carbonate, of the present invention are attained at above 100 fold of this concentration (~2-3 wt.%, based on $CaCO_3$).

Other factors may indicate use of even higher concentrations of the active agent in the production process of the present invention. For instance, coating the surface of the particulate precipitated aragonite, with a predetermined rather thick layer of the active agent, *in situ*, in a carbonator/flotation cell, may require quite high concentrations of this material, which may exceed 5%, 10% and even 15 wt.%, based on $CaCO_3$, in order to produce good surface coated hydrophobic and acid resistant particulate precipitated aragonite (e.g. for master batches). Naturally, at such high active agent concentrations, the cost component of the coating should then be compared to the alternative possibilities of downstream coating, which are also available in the prior art, as well as in the present invention (c.f. figs. 1 and 2, respectively). Another serious reason to avoid operating the process at too low concentrations, is the fact that the chemical and physical properties of the product, and especially its optical properties and specific gravity, which are quite interdependent, are dramatically affected by the concentration of the active agent.

In between the upper limit and the threshold limit of the concentration of the active agent in the process of the present invention, the optimum concentration should also be determined by one skilled in this art, either vis-a-vis the quality of the $CaCO_3/CaO$, or whenever the properties of the product are to be changed. The active agent is not an expensive material, but still it may throw an economical burden on the total cost of the final product due to the fact that even quite pure particulate precipitated aragonite is a relatively inexpensive material.

Intuitively, the concentration of 10 wt.%, based on the calcium carbonate, seems to be an economical upper limit of the active agent, while 0.2 wt.%, wt; based on the $CaCO_3$, seems to be its threshold (minimum) concentration.

<u>Carbon Dioxide in the Carbonation Step</u>

Use of carbon dioxide gas or a carbon dioxide containing gas is well known in the prior art methods for producing precipitated calcium carbonate particles. The process of the present invention is similar in this respect to the prior art processes that operate with substantially pure carbon dioxide gas as well as with mixtures of carbon dioxide with up to about 92 v% inert gases (e.g. air). At lower concentrations of the carbon dioxide in the feed

gas (<8 wt.%), however, the efficiency of the process may be too low, mainly, due to the cooling effect of the excessive gas.

In order to understand how to control the process of the present invention, it is worthwhile to describe the major effects that are observed at the two limits, namely, when using "rich" feed gas of about 100% carbon dioxide on the one hand and using "lean" feed gas of about 8 v% carbon dioxide on the other hand. It was found that "rich" carbon dioxide gas feed leads to a PCC, of the present invention, that gives rise to products of much higher gloss than those that are produced from the PCC, of the present invention, that are produced with a "lean" carbon dioxide feed under similar production conditions. Namely, the gloss of the final (consumer) products can easily be fine-tuned by just choosing the right CO_2/inert gas (air) ratio. This fact may be exploited, especially, in using the product of the present invention in formulations that are intended to be used e. g. in the coating industry, which requires quite often low gloss products and in the paper industry for coating paper and obtaining a desirable product of high gloss.

Another phenomenon that is observed when using "lean" feed gas is that it leads to a PCC, of the present invention, of lower specific gravity and of higher hiding power, compared to a PCC, of the present invention, that is produced with "rich" feed gas under similar conditions. That, in turn, allows to include carboxylic acids within the patent range, which otherwise could not meet the constrains that were set up to determine which carboxylic acid is within the borders of this invention and can be used as an active agent to produce the product of the present invention. For instance, under the conditions of the screening test (Example 1; that is described hereinafter), Lauric acid could not be considered active agents (its product was considered "Calcite" as its crystallographic purity (aragonite/(aragonite+calcite)) was only 20%-25% and its specific gravity (in tall oil; after drying it at 120°C for twelve hours) was only 2.54 g/cm^3. When using a "lean" feed gas of 26% CO_2 (by volume) the specific gravity of the product decrease dramatically to 1.78 g/cm^3. Therefore, based on the too high specific gravity values that were obtained for lauric acid, for palmitic acid and for stearic acid, the myristic acid was not considered, at that time, to be a viable candidate to catalyze the process of the present invention and ,thus, due to the time constrains, it was not tested and not included in Table 1. The use of very "lean" gas feed allows to sort out and use much more carboxylic acids (lauric acid, myristic acid and even stearic acid) to serve as the active agents of the process of the present invention, using the simple and straight forward methods that were developed herein

Additives in the Process:

The process of the present invention is quite self-sufficient and requires only the active agent in suitable quantities, as discussed above. The active agent can be introduced preferably already premixed with the aqueous calcium hydroxide slurry, or alternatively (or additionally) it can be introduced directly into the carbonator. The active agent can also be used downstream the carbonation stage, but that, naturally, has no effect on the production of the particulate precipitated calcium carbonate, and particularly the particulate precipitated aragonite, in the carbonator.

It appears that the active agent has a surprising affinity to the aragonite, which is unlikely to be adversely affected by the presence of other additives. Consequently, additives like phosphoric acids and water soluble salts thereof, can be used in the present invention to modify the product properties by increasing the aspect ratio of the thus formed acicular crystals; polyacrylates, polyacrylamides and some short-chain carboxylic acids can be used to modify the rheology of the product mixtures and allow operation at higher calcium hydroxide concentrations and, consequently, at higher throughputs; chelating agents can be used to convert heavy metals into water-soluble species and once again lead to super-pure products; metal powders and carbon black may be introduced to obtain electrically conductive powders; soluble aluminum salts may affect the shape of the calcite particles; and magnesium salts or preferably $MgO/Mg(OH)_2$ may lead to hydromagnesite. The prior art is infested with examples of additives that are used to achieve improved particulate calcium carbonate products. These additives and many others may, potentially, be used in the product (process) of the present invention.

It is nevertheless prudent to check carefully the effect that well known additives of the prior art may have on the action of the active agent, but in most cases the active agent will be the dominant catalyst for the purpose of the present invention and, therefore, such additives can usually be introduced at various stages of the process, as is customary in the prior art (c.f. Figs. 1 and 2).

The Mixing System

The need for high shear mixing in this process is well known in the relevant art. The mixers may be a rotor/stator type or a rotor only type. Usually, the latter one is used to produce relatively larger product particles, while the rotor/stator type leads to much higher attrition of the acicular crystals. On the other hand, the rotor/stator type may allow a more efficient dispersion of the gas bubbles, thereby improving the quality of the product. The skilled operator will utilize the preferred mixing system for working or enhancing the present

process. The type of mixers and the rotor speed should be optimized according to the desired carbonation performance and the desired product characteristics.

The lower limit of the rotor speed (hereinafter - "Tip Speed" or "Peripheral Speed") is known in the prior art. A requirement of a minimum tip speed of about 5 m/sec., to effect the formation of desired product is not unusual in this art.

The upper limit of the rotor speed is determined by mixer technology, cost of the specific mixer, the nature of the desired product and the energy that is to be used. For instance, the higher the rotor speed, the lower may be the reaction time (in a continuous process, the reaction time is termed HUT (Hold Up Time) and it is calculated as follows: HUT = V (the carbonator volume) / F (the discharge rate of the product mixture out of the carbonator)). This in turn may lead to small particles. A skilled person in this art will know how to optimize the kind of mixers and rotor speeds above the minimal peripheral speed, which is preferably 5 m/sec.

The Reaction Duration in the Reactor/Carbonator/Flotation Cell

As already mentioned above, the carbonation step is preferably conducted in a continuous mode of operation. In such a case, "reaction duration" is hardly relevant, but we can calculate the HUT (Hold Up Time), which lies essentially within the range between 5 minutes and 180 minutes. At below the lower limit of the HUT the yields may be too low and the PSD (Particle Size Distribution) of the product may be too small, while at the upper limit of the HUT the process throughput may be too low, the yields may be excellent and the PSD may be too small, because of excessive attrition of the product in the flotation cell. Once again, the skilled person will be able to determine by experiment, suitable working parameters vis-a-vis the desired product properties and to optimize its quality and cost.

The Specific Gravity and the Loose Bulk Density (L.B.D.) of the Particulate Precipitated Calcium Carbonate of the Present Invention

The specific gravity of the PCC of the present invention is measured for the following three major reasons: (a) to distinguish the product of the present invention from the products of the prior art; (b) to distinguish the process of the present invention from the processes of the prior art; and (c) to control and optimize the process and the product of the present invention. More specifically, the specific gravity of the product of the present invention, after igniting it at 500°C for eight hours, as is described in Example 14

hereinafter, is the most decisive and accurate criterion to determine that the relevant product has a specific gravity of <2.5 g/cm^3 (preferably <2.3 g/cm^3 and more preferably <2.1 g/cm^3) and, therefore, it is indeed the product of the present invention. Therefore, also the process that produced such a product is the process of the present invention. The total elimination of the carboxylates from the PCC particles after such a thermal treatment (N.D. i. e. <1ppm; as measured by GC-MS analyses), circumvents the problem of adhering gas bubbles onto the surface of the measured PCC samples, and thus the specific gravity values for products of the prior art (calcite, as well as, aragonite) are always >2.5 g/cm^3 (even >2.65 g/cm^3), while the products of the present invention are characterized, by definition as such, by their specific gravity values <2.5 g/cm^3 (preferably <2.3 g/cm^3 and even more preferably <2.1 g/cm^3).

However, the PCC particles are usually being used in practice without any such a drastic ignition treatment (at 500°C for 8 hours) and in most cases the PCC particles are even not being dried, but rather dispersed in water, after the dewatering step, using known dispersants to obtain stable dispersions (slurries of >50 wt%). Therefore, the PCC particles of the prior art may be coated with carboxylates, and therefore, they may be surrounded by gas (usually air) bubbles that lead to a seemingly "reduced" specific gravity, of which value is substantially below 2.5 g/cm^3. However, this erroneous situation last only until these PCC particles are subjected to high shear forces (e. g. in the processes of making coatings, inks and paper) that causes the separation of these gas bubbles, unless they are "hidden" deep below the surface of the PCC particles, and that is the basis of the present invention. Therefore, any suggestion that is made herein to measure the specific gravity of the PCC particles, after drying them at 120°C for 12 hours only, is just to get the notion that indeed the respective product may be of suitable properties and be further ignited at about 500°C for the time that is necessary to remove all the organic moieties, before further specific gravity tests are conducted. A person skilled in the art may choose other conditions to perform this task, but then he should make sure that the organic compounds are no longer in/onto the tested PCC particles.

Contrary to what was thought before, that the "pores" in the PCC particles of the present invention are closed, we know now that these "pores" are semipermeable (or selectively permeable) to liquids and gases. Any attempt to use the regular gas phase pycnometer measurements to determine the specific gravity of commercial PCC particles, as well as the PCC of the present invention, will lead to values above 2.5 g/cm^3, irrespective of the kind and source of these calcium carbonate products or the kind of

treatment that these samples received prior to the specific gravity analyses (c. f. Example 14 (D)). Namely, using such a practice would have resulted in totally overlooking the present invention. However, conducting specific gravity analyses of the PCC particles of the present invention (after treatment at 500°C for eight hours) in liquids like water, oleic acid (>97%), cold pressed edible olive oil, refined edible sunflower oil, refined edible corn oil, refined edible soybeans oil, refined canola oil, and tall oil, leads to values <2.5 g/cm^3 (preferably <2.3 g/cm^3 and more preferably <2.1 g/cm^3). Similar measurements of the specific gravity of commercially available GCC (calcite) and PCC (calcite and aragonite) gave always rise to values that were >2.5 g/cm^3 (even >2.6 g/cm^3 and even >2.7 g/cm^3). When the measurements of the specific gravity were conducted in water, the specific gravity of the products of the present invention were <2.5 g/cm^3, but however, when a small amount of sodium dioctylsulfosuccinate (2%) was added to the slurry, the specific gravity of the PCC particles increased quite fast and ended up at values >2.7 g/cm^3 (such a phenomenon could not be observed in the case of the prior art GCC or PCC products). This phenomenon of penetration of liquids into the "pores" of the product of the present invention has a lot of benefits, but when this happens on preparing the usual stable slurries of PCC (of >50 wt%) by mixing the PCC, water and a suitable dispersants, it results in a very thick, high viscose mass. At the preparation stage, PCC slurries made of a product of the prior art look, superficially, quite similar to those that are made of the product of the present invention, but this superficial appearance may mislead. For instance, measuring the specific gravity (S.G.) of the PCC particles of the prior art will result in values that are > 2.5 g/cm^3, while the S.G. of the PCC particles of the present invention will be considerably lower values. Moreover, the addition of a wetting agent, like the sodium dioctylsulfosuccinate, to these slurries will reveal a much more dramatic behavior. Namely, such slurries of the PCC particles of the prior art may not be affected much, but the slurries made of the PCC particles of the present invention will turn into a dense and thick high-viscose mass and the S.G. values of the particles therein will increase to > 2.7 g/cm^3, due to the penetration of the aqueous phase into the PCC particles.

Due to the fact that the "pores" in the products of the present invention are not closed to gases and to some liquids, it is important to avoid the customary gas pycnometer specific gravity (S. G.) measurements when analyzing the product of the present invention, and rather follow the exact instructions of how to do it (c. f. in Example 14 and especially in Example 14 (F)). These measurements reveal best the desired properties of the novel products of the present invention and of the process of the present invention and give a

close picture of how these PCC particles are going to improve the final (consumer) products, due to their unique property – "porosity".

Another observation can be made, based on the experimental data that was collected thus far, that the loose bulk density (L.B.D.) of the products of the present invention have remarkably lower values (<0.5 g/cm^3 and even <0.4 g/cm^3), than those of similar products of the prior art (usually > 0.5 g/cm^3). Therefore, we may also use this phenomenon to serve as an additional criterion to indicate whether a product of such low L.B.D. is in the domain of the present invention. The exact procedure of how to perform this test will be detailed in Example 14 (G). Generally, particulate PCC products, previously dried at 120^{o}C for twelve hours, that are of SSA (Specific Surface Area) (BET) ≤ 13 m^2/g will belong to the domain of the present invention if they have a L.B.D. of less than 0.4 g/cm^3, provided that they are coated by e.g. decanoic acid, dodecanoic acid, myristic acid, undecylenic acid, stearic acid and alike carboxylic acids that are used as the active agent in the particular case, as instructed in Example 14 (G). Products of higher SSA will not be tested according to this L.B.D. test, but rather by only the S.G. test, as instructed in Example 14 (F).

The present invention will now be described in more detail by way of Examples, which are presented for illustration purposes only and are not be construed restrictively.

Experimental:

Raw Materials:

A. All raw materials were purchased from Aldrich, unless otherwise specified.

B. Ethyl decanoate was prepared by reacting decanoyl chloride with ethanol in the presence of triethylamine at about 50°C. After about 3 hours the product was washed with water to remove water-soluble residues and it was then dried at about 50°C under a vacuum of about 30 mm/Hg.

C. Sodium decanoate was prepared by thoroughly mixing decanoic acid with 2% aqueous NaOH at about 70°C until the pH passed 10.

D. Potassium decanoate was prepared by thoroughly mixing decanoic acid with 2% aqueous KOH at about 70°C until the pH passed 10.

5th. CaO(1) - of Arad, Israel.

6th. CaO(2) - of Shfeya, Israel.

G. Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.

H. CO_2 - Cylinders of 100 % pure compressed gas of Mifalay Hamzan Ltd., Haifa.

I. Tall Oil (Sylvatal 20S) of Arizona Chemical, USA.

J. Ultrafine stearic acid coated GCC – Omya UFT 95 ex Omya-Pluess-Staufer - Switzerland.

K. A commercial ultrafine stearic acid coated - Ultraflex PCC ex SMI - USA.

L. A commercial ultrafine talc – Ultratalc 609 ex SMI - USA.

M. Isostearic Acid - Emersol 875 ex Henkel - Germany.

N. The Paint Constituents:

Nopco NDW of Henkel

Cellosize QP 15000 (hydroxy ethyl cellulose) of Union Carbide

Disperse One (45% N.V.) of Tambour, Israel

Synperonic NP10 of ICI

TiO_2 (Kronos 2160) of Kronos (However, similar TiO_2 pigments, like Tioxide R-TC90 and Tioxide TR92, of which their D_{50}= 220 nm ± 20 nm may serve equally well)

Synthetic sodium aluminum silicate (p820) of Degussa

Kaolin clay (D_{50} = 3.1 micron) of Engelhard

$CaCO_3$ powder (d_{50}=3.5 microns) of Polychrom, Israel - "Girulite-8"

Talc (D_{50} = 12.3 micron) of Lusenac Val Chisone

Copolymer vinyl acetate acrylate emulsion (55% N.V.) of Cerafon, Israel

Butyl diglycol acetate of Union Carbide

Kathon LXE of Rohm & Haas

Ammonia (25%) of Frutarom, Israel

Antioxidant (Irganox B225 ex Ciba Specialty Chemicals - Switzerland)

Lubricant (Wax PE 520 ex Hoechst-Celanese - USA)

Polypropylene copolymer (Capilene-TR50 ex Carmel Olefins - Israel).

Instruments and Accessories:

1. pH meter/controller; Jenco; Model 3671; Made in China.
2. pH electrode; Hanna Industries; type HI 1131B (Glass Probe).
3. Thermometer; Jenco Model 3671; Made in China.
4. Peristaltic pump; Watson-Marlow; Model 505u (variable speed).
5. Agitator; Ika; Model RW-20 (variable speed).
6. Dissolver; Hsiangtai; Model HD-550; Made in Taiwan
7. Ultra-turrax® T50; Ika; rotor d = 3.8 cm; stator d = 4 cm.
8. Disk type rotor of d = 12 cm.
9. Disk type rotor of d = 8 cm.
10. Saw-blade type rotor of d = 9 cm.
11. Saw-blade type rotor of d = 4.8 cm.
12. Hydrocyclone 2``; Mozely; P = 50 psi; vortex finder = 11 mm; spigot = 6.4 mm.
13. Vacuum pump; Vacuumbrand GmbH; Model MD 4C.
14. Buchner + filter cloth with 8-10µm pores.
15. XRD (X - Rays Diffractometer); Siemens D-500 for the crystallographic phases.

16. SEM (Scanning Electron Microscope); Jeol 5400 for the shapes of the particles.

17. Colorimeter; Hunterlab D25-PC2 for whiteness measurements.

18. Colorimeter; ACS instrument (Applied Color Systems).

19. Ultrasonic bath (10 l); Selecta, Spain - "ULTRASONS".

20. Ultrasonic cleaners (baths) of limited power (<100 Amp.Volt.) e.g. P-08890-01/06 ex Cole Parmer – USA.

21. Analytical Balance; Shekel Ltd., Israel.

22. HPLC Analyzer; Waters HPLC Analyzer (Detector 486 + Autosampler 717 + Pump 510 + millenium Software).

23. . HPLC Column; Phenomenex C18(250 mm x 4.3 mm; 5µm Particle size).

24. AccPyc 1330 ex Micromeritics – USA.

25. Glossmeter (Minigloss 101N ex Sheen Instruments – England).

26. Reflectometer (Ref. 310 Sheen-Opac ex Sheen Instruments – England).

27. Twin-screw compounder (L/D = 24 ex Dr. Collin – Germany).

28. Injection machine (25 t ex Dr. Boy – Germany).

29. Screen-shaker (Rotap Model RX-29-10 ex W.S. Tyler Inc. – USA).

30. GC-MS for trace analysis - of HP Model 5890/5971

PREPARATION I - Preparation of Aqueous Calcium Hydroxide Slurries:

The aqueous calcium hydroxide slurry was prepared in the laboratory in a batch mode of operation as follows: 40 kg of tap water were introduced into a 50 l. stainless steel 316 reactor that was equipped with a steam heated jacket, a thermometer and with the Haiangtal Dissolver with a rotor of d = 12 cm. The Dissolver was operated at 200 rpm, 4 kg of CaO (Shfeya) were added to the reactor during less than 10 minutes and the slurry was allowed to stir for 10-80 minutes. At that time the temperature rose to above 60°C and when it reached its maximal temperature at 80-90°C, the mixture was ready for its purification prior to the carbonation stage, as follows:

a. The slurry passed a stainless steel 316 screen to remove particles of d > 2 mm, and

b. The filtered slurry passed a hydrocyclone to remove particles of d > 50 µm.

Notes:

At this point the warm aqueous calcium hydroxide slurry was ready for its use in the carbonation stage and its temperature was maintained at a preset value by heating the slurry in the above reactor in order to control the temperature in the carbonator.

The potential active agent(s) and any optional additives could be blended into the warm slurry at a preset concentration before the purification steps a. and b. or thereafter.

This batch mode of operation is used only in the laboratory tests. The production plant is intended to be operated under a continuous mode of operation, as is discussed herein.

PREPARATION II - Preparation of Aqueous Calcium Hydroxide Slurries:

PREPARATION I was repeated using CaO of Arad, a substantially purer raw material than that of Shfeya (the respective whitenesses are >95% and ~88%).

EXAMPLE 1 - Screening Test for the Potential Active Agents:

Possible active agents were investigated by producing particulate precipitated calcium carbonate according to the following procedure:

2 kg tap water were added to a 3.2 l. stainless steel 316 reactor (of inner diameter d = 15 cm and length – 18 cm), equipped with a steam heated jacket, a pH electrode, a thermometer and the Halangtal Dissolver with a saw-blade rotor of d = 4.8 cm (c.f. Fig 3). The Dissolver was operated at a preset speed and carbon dioxide gas or a carbon dioxide containing gas and the aqueous calcium hydroxide slurry of PREPARATION I, containing already the active agent, were fed simultaneously into the reactor, while maintaining the pH, the temperature and the production rate at preset values. The product was collected at the top of the reactor, and the impurities were discharged from the bottom of the reactor (naturally, the product exited from the bottom of the

reactor when the experimental active agent did not lead to a particulate precipitated aragonite and to its flotation).

The first 10 l. of resulting slurry were discarded. The residual slurry was collected and it was filtered through a filter-cloth on the Buchner using a vacuum pump to dewater the product. The filter cake was dried for 12 hours at 120°C and the crystallographic morphologies and the shapes of the crystals of the precipitated calcite and/or aragonite calcium carbonate particles were determined using XRD and SEM analyses, respectively. The results are shown in the Table 1, below.

<u>The process set points - continuous mode of operation:</u>

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10m/sec.).
2. pH = 9.5.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).
6. Potential active agent concentration = 1 wt.%, based on $CaCO_3$.

Table 1- the results of EXAMPLE 1

Test #	Active Agent	Number of Carbons	Product (Isomorph)
1	Propionic acid	3	Calcite
2	Lactic acid	3	Calcite
3	Pyruvic acid	3	Calcite
4	Acrylic acid	3	Calcite
5	Methoxyacetic acid.	3	Calcite
6	Methacrylic acid.	4	Calcite
7	Butanoic acid	4	Calcite
8	Pentanoic acid	5	Calcite
9	Hexanoic acid	6	Calcite
10	Heptanoic acid	7	Calcite
11	Octanoic acid	8	Calcite
12	Phthalic acid	8	Calcite
13	Terephthalic acid	8	Calcite
14	2-Ethylhexanoic acid	8	Calcite
15	Nonanoic acid	9	Aragonite
16	Nonanoic acid *	9	Aragonite
17	Azelaic acid	9	Calcite
18	Trimelitic acid	9	Calcite
19	Decanoic acid	10	Aragonite
20	Decanoic acid *	10	Aragonite
21	Sodium decanoate	10	Aragonite
22	Potassium decanoate	10	Aragonite
23	Ethyl decanoate	12	Aragonite
24	Decanoyl chloride	10	Aragonite
25	Decanoic acid anhydride	20	Aragonite
26	Undecanoic acid	11	Aragonite
27	Undecanoic acid*	11	Aragonite
28	4-Butylbenzoic acid	11	Calcite
29	Dodecanoic acid**	12	Calcite
30	Palmitic acid	16	Calcite
31	Stearic acid	18	Calcite
32	Oleic acid	18	Calcite
33	$MgCl_2$	-	Calcite
34	$AlCl_3$	-	Calcite
35	$C_{12}H_{25}C_6H_4SO_3H$ (LABSA)	18	Calcite

* - Was pumped continuously and directly into the carbonator.

** - This experiment led to mostly calcite (of a crystallographic purity (aragonite/(aragonite+calcite)) ~20%-25%) and to a specific gravity (S. G.)=2.54 g/cm3 (measured according to Example 14A), which is outside the limits of the present invention (S. G. < 2.5 g/cm3). However, the use of CO2 containing gas (26% by volume CO2 and 74% by volume Air) and 1.5% dodecanoic acid in an experiment similar to that described in Example 10, led to a product of mostly aragonite (of a crystallographic purity (aragonite : (aragonite + calcite)) >50%) and to a specific gravity (S. G.)=1.78 g/cm3 (measured according to Example 14A).

EXAMPLE 2 - a Screening Test for Interfering Compounds:

EXAMPLE 1 was repeated, except that in all the experiments 1% (wt; based on the calcium carbonate) decanoic acid was premixed in the aqueous calcium hydroxide slurry feed and in each experiment an additional experimental active agent was added to study its effect on the activity of the decanoic acid. The results are shown in Table 2, below.

The process set points - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.)
2. pH = 9.5.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agents concentrations = 1 wt.% decanoic acid + 1 wt.% potential active agent based on $CaCO_3$.

Table 2- the results of EXAMPLE 2

Test #	Active Agent	Number of Carbons	Product (Isomorph)
1	Propionic acid	3	Aragonite
2	Lactic acid	3	Aragonite
3	Pyruvic acid	3	Aragonite
4	Acrylic acid	3	Aragonite
5	Methoxyacetic acid	3	Aragonite
6	Methacrylic acid	4	Aragonite
7	Butanoic acid	4	Aragonite
8	Pentanoic acid	5	Aragonite
9	Hexanoic acid	6	Aragonite
10	Heptanoic acid	7	Aragonite
11	Octanoic acid	8	Aragonite
12	Phthalic acid	8	Calcite
13	2-Ethylhexanoic acid	8	Aragonite
14	Nonanoic acid	9	Aragonite
15	Azelaic acid	9	Aragonite
16	Trimellitic acid	9	Calcite
17	Decanoic acid	10	Aragonite
18	Undecanoic acid	11	Aragonite
19	4-ButylBenzoic acid	11	Aragonite
20	Dodecanoic acid	12	Aragonite
21	Palmitic acid	16	Aragonite
22	Stearic acid	18	Aragonite
23	Oleic acid	18	Aragonite
24	$MgCl_2$	-	Aragonite
25	$AlCl_3$	-	Aragonite
26	$C_{12}H_{25}C_6H_4SO_3H$ (LABSA)	18	Aragonite

EXAMPLE 3 - A Batch Mode of Operation:

A batch mode of operation, of which parameters were as close as possible to those of EXAMPLE 1, was attempted. Only particulate precipitated calcite of rhombohedral shape was obtained. No particulate precipitated aragonite could be obtained when using decanoic acid or any other active agent that was mentioned as being effective in EXAMPLE 1. The experiment was conducted as follows:

The active agents were investigated by producing precipitated calcium carbonate particles according to the following procedure:

2 kg aqueous calcium hydroxide slurry, containing already the respective active agent (c.f. EXAMPLE I) were added to the 3.2 l. stainless steel 316 reactor of EXAMPLE 1. The Dissolver was operated at 4000 rpm, the

temperature was maintained at 85°C and the production rate was determined by controlling the feed rate of the carbon dioxide gas. The carbonation was stopped after about 20-30 minutes, when the pH reached 7. The product mixture was then removed from the reactor through its bottom outlet.

The resulting slurry was filtered through a filter cloth on the Buchner using a vacuum pump to dewater the product. The filter cake was dried for 12 hours at 120°C and the crystallographic morphologies and the shapes of the crystals of the precipitated calcite particles were determined using XRD and SEM analyses, respectively. As mentioned above, no precipitated aragonite particles were obtained.

The process set points - batch mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10m/sec.).
2. pH = ~14 → 7.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = 2 kg.
6. Potential active agent concentration = 1 wt.%, based on $CaCO_3$.

EXAMPLE 4 - Parametric Studies - the Effect of the Temperature:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = variable.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the p
6. Active agent concentration = decanoic acid; 0.5 wt.%, based on $CaCO_3$.

Table 3- the results of EXAMPLE 4

Test #	Temperature °C	Mineralogical Phase XRD
1	87	Aragonite
2	80	Aragonite
3	70	Aragonite
4	60	Aragonite
5	50	Calcite

EXAMPLE 5 - Parametric Studies - Effect of the pH:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = variable.
3. Temperature = 87°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour)
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
5. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 4- the results of EXAMPLE 5

Test #	pH	Mineralogical Phase XRD
1	10	Aragonite
2	9.5	Aragonite
3	9	Aragonite
4	8.5	Aragonite
5	8.0	Calcite
6	7.0	Calcite

EXAMPLE 6 - Parametric Studies - Concentration Effect of the Active Agent

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = 87°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; variable wt.%; based on $CaCO_3$.

Table 5- the results of EXAMPLE 6

Test #	Decanoic acid % (wt)	Mineralogical Phase XRD
1	1.0	Aragonite
2	0.5	Aragonite
3	0.3	Aragonite + Calcite*
4	0.2	Aragonite + Calcite*
5	0.1	Calcite

* - A crystallographic purity (aragonite/(aragonite + calcite)) <90%.

Note: Though the present invention is especially aimed at obtaining substantially pure particulate precipitated aragonite calcium carbonate of crystallographic purity (aragonite phase/(aragonite phase + calcite phase)) ≥90% and even >95%, there are still applications that can utilize mixtures of these isomorphs where such crystallographic purity is <90%, and such mixtures are within the scope of the present invention. In such cases the boundary conditions of the present invention (c. f. Tests #3 and #4, above) may still be used.

EXAMPLE 7 - Parametric Studies - Concentration Effect of the $Ca(OH)_2$

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12m/sec.).
2. pH = 9.5.
3. Temperature = 87°C .
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour)

5. Aqueous calcium hydroxide slurry (of Shfeya) -variable wt.% = – variable L.P.H. (to maintain the preset pH value).

6. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 6- the results of EXAMPLE 7

Test #	Solids in Slaked Lime % (wt)	Mineralogical Phase XRD
1	8	Aragonite
2	4	Aragonite
3	3	Aragonite + Calcite*
4	2	Aragonite + Calcite*
5	1	Calcite

* - A crystallographic purity (aragonite : (aragonite + calcite)) <90% and c.f. the above note at the end of Example 6.

EXAMPLE 8 - Parametric Studies - Rotor Speed Effect:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = variable rpm (Tip Speed ~ variable).
2. pH = 9.5.
3. Temperature = 87°C.
4. Carbon dioxide flow rate = 180 L.P.H (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 7- the results of EXAMPLE 8

Test #	Rotor Speed rpm	Tip Speed m/sec.	Mineralogical Phase XRD
1	10000	25	Aragonite
2	4800	12	Aragonite
3	2000	5	Aragonite + Calcite*
4	1000	2.5	Calcite

* - A crystallographic purity (aragonite : (aragonite + calcite)) <90% and c.f. the above note at the end of Example 6.

EXAMPLE 9 - Parametric Studies - Effect of the CO_2 Flow Rate (F.R.)

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = 87°C .
4. Carbon dioxide flow rate = variable L.P.H. (liters/hour)
5. Aqueous calcium hydroxide slurry (of Shfeya) -variable wt.% = ~ variable L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 8- the results of EXAMPLE 9

Test #	CO_2 Flow Rate L.P.H.	Mineralogical Phase XRD
1	240	Aragonite
2	180	Aragonite
3	120	Aragonite

EXAMPLE 10 - Parametric Studies - Effect of the CO_2/Air Ratio:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = 87°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5 wt.%; based on $CaCO_3$.
7. Air = variable.

Table 9- the results of EXAMPLE 10

Test	Air/CO_2	Mineralogical Phase

#		XRD
1	0	Aragonite
2	0.33	Aragonite
3	0.66	Aragonite

EXAMPLE 11 - The Effect of Active Agent on Content of the Wet Filter Cake:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The content of $CaCO_3$ in the wet filter cake was determined after drying 12 hours at 120°C. Relatively pure (aragonite phase/(aragonite phase + calcite phase)) ≥95% and dry precipitated acicular aragonite calcium carbonate particles were obtained. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = 90°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.7; 1.0; 2.0 wt.%; based on $CaCO_3$.

Table 10- the results of EXAMPLE 11

Test #	Dosage % (wt)	Product (Isomorph)	$CaCO_3$ % (wt)*	Crystallographic Purity**
1	0.7	Aragonite	>80	≥95%
2	1.0	Aragonite	>80	≥95%
3	2.0	Aragonite	>80	≥95%

* - % (wt) $CaCO_3$ = 100 x wt. of dry filter cake / wt. of wet filter cake

** - As determined by the XRD analyses (for Test #2 - c.f. Figs. 4 and 5)

Note:

By choosing relatively standard conditions for the present process, it is possible to reduce the water content in the wet filter cake below 20 wt.%.

EXAMPLE 12 - The Effect of the Active agent on the Resistivity to Acids:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only, the resistivity of the dry samples to acidic aqueous solutions being

determined as follows. A 5 l. solution of HCl in water at pH=3.5 was prepared for all the following experiments, so as to assure equal starting experimental conditions. 100 ml of this HCl solution were poured into a 100 ml graduated cylinder, 5 g of precipitated $CaCO_3$ particles were added and the pH was measured after 20 minutes. Evolution of CO_2 was observed visually, as was the behavior of the commercial sample #C, the calcite #BM-37, and it was found that the aragonite samples of the present invention (#12-3, #12-4, #12-5) were markedly different. It is worthwhile to note that sample #12-5 produced few bubbles that did not detach from the surface of the precipitated aragonite particles. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 5200 rpm (Tip Speed ~ 13 m/sec.).
2. pH = 9.5.
3. Temperature = 90°C.
3. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
4. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
5. Active agent concentration = decanoic acid; 0.7%; 1.0 %; 2% wt.% based on $CaCO_3$.

Table 11- the results of EXAMPLE 12

Test #	Sample #	Active agent (wt.%)	Product (isomorph)	pH after 20 mins.	Note
1	C*	Unknown	Aragonite	>8	Violent Evolution of CO_2
2	BM-37**	1.0	Calcite	>5	Evolution of CO_2
3	12-3	0.7	Aragonite	<4	Slight Evolution of CO_2
4	12-4	1.0	Aragonite	<4	Slight Evolution of CO_2
5	12-5	2.0	Aragonite	<4	No Evolution of CO_2

* - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40

** - This sample was taken from the batch mode of operation in EXAMPLE 3

Note:

By choosing relatively standard conditions for the present process, it is possible to increase the resistance of the product towards acids by using quite low concentrations of the active agent and obtain excellent product for the

paper industry of which processes are acidic and for the coating industry for durable paints for acidic environments.

EXAMPLE 13 - Effect of Raw Material/Process on Whiteness of the Product:

EXAMPLE 1 and EXAMPLE 3 were conducted using the aqueous calcium hydroxide slurries of PREPARATION I and of PREPARATION II for comparison. The whitenesses of the products are compared.

The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.).
2. pH = 9.5.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour)
5. Aqueous calcium hydroxide slurry (of Arad/Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 1 wt.% based on $CaCO_3$.

The process set points - batch mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.).
2. pH = ~14 → 7.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Arad/Shfeya) - 10 wt.% = 2 kg.
6. Active agent concentration = decanoic acid 1 wt.% based on $CaCO_3$.

Table 12 - the results of EXAMPLE 13

CaO of Arad (whiteness = >95%)		CaO of Shfeya (whiteness = ~88%)	
Continuous	Batch	Continuous	Batch
AR-83A	BM37A	AR-83	BM37
Aragonite $CaCO_3$	Calcite $CaCO_3$	Aragonite $CaCO_3$	Calcite $CaCO_3$
Whiteness=98-9%	Whiteness=97-8%	Whiteness=97-9%	Whiteness=92-5%

Notes:

1. When the raw material (CaO) is relatively pure, the whiteness of the products (AR-83A and BM37A) is not (and should not be) much different. However, when the CaO is relatively impure, the whiteness of the precipitated aragonite particles (AR-83) is dramatically higher than the corresponding calcite (BM37), due to the unique effect of the process of the present invention.

2. The whiteness of the precipitated particulate aragonite obtained according to the present process attains top quality, independently of the calcium hydroxide source.

EXAMPLE 14 – Effect of the Active Agent/Process on the Specific Gravity (S.G.) of Precipitated Particulate Calcium Carbonate:

EXAMPLE 1 was repeated using the aqueous calcium hydroxide slurry of PREPARATION I, except that the concentration of decanoic acid was gradually increased.

(A) Determination of the Specific Gravity (S.G.) in Tall Oil of a Product Dried at 120°C

1. The wet filter cake of the $CaCO_3$ sample was dried for 12 hours at 120°C to remove all free water.

2. A weighed quantity of the dry $CaCO_3$ sample (Wc) + a weighed quantity of tall oil (Wo) (Density of 0.93 g/cm^3) were introduced into a 1 l. glass beaker.

3. The mixture was stirred with the Hasiangtai HD-550 Dissolver for 10 minutes, at 4000 rpm (using a saw-blade rotor of d = 4.8 cm).

4. The slurry was poured into a 250 ml graduated glass settling column and was sonicated gently in an ultrasound bath for 20 minutes, until all the visible trapped bubbles were released from the surface of the PCC particles. In order not to destroy the structure of the "porous" product of the present invention while sonicating it, thereby leading to higher S.G. values, the use of ultrasonic cleaners (baths) of limited power (<100 Amp.Volt.) e.g. P-08890-01/06 ex Cole Parmer – USA, is recommended.

5. The settling column was then evaluated at 20-22°C for:

(a) the volume of the slurry - V

(b) the total net weight of the slurry - W

Based on the above measurements, the following was calculated:

(1) from the equation: D = W/V g/cm^3, the density of the slurry;

(2) from the equation

1/D = [Wc(Wo + Wc)]/S.G. + [Wo(Wo+Wc)]/0.93,

the S.G. of the $CaCO_3$ sample was calculated.

6. The loose bulk density (B.D.) of the dry powder was measured using a balance and a graduated cylinder.

The process set points - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.)
2. pH = 9.5.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5; 1; 2; 5; 2; 1 wt.% based on $CaCO_3$.

The results are as follows:

Table 13 - the results of EXAMPLE 14 (A)

Test #	Sample Code	Active agent	Dosage (wt.%)	Mineralogical Phase XRD	S.G.† g/cm³	Loose B.D.† g/cm³
1	Natural $CaCO_3$	-	-	Calcite	2.63	0.65
2	BM-37*	decanoic acid	1	Calcite	2.54	0.37^BM
3	C**	N.A.	N.A.	Aragonite	2.56	0.54
4	AR-81	decanoic acid	0.5	Aragonite	2.02	0.31
5	AR-83	decanoic acid	1	Aragonite	1.90	0.30
6	AR-118	decanoic acid	2	Aragonite	1.75	0.25
7	AR-119	decanoic acid	5***	Aragonite	1.67	0.29
8	AR-135	nonanoic acid	1	Aragonite	1.88	0.31
9	AR-120	decanoic acid	2^	Aragonite	1.72	0.23

* - The sample was taken from the batch mode of operation in - EXAMPLE 3.
** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.
*** - 5g of AR-119 were dissolved in a 10% HCl solution. The decanoic acid was extracted with 1,2-dichloroethane. HPLC analysis using a C18 column revealed 4.93% (wt; based on the calcium carbonate) of this acid in the sample.
^ - 50ppm of phosphoric acid were used in addition to the decanoic acid to increase the aspect ratio of the acicular aragonite.
† - A dry powder after drying for 12 hours at 120°C.
BM – The relatively low L.B.D. of this product should not be compared to the other L.B.D. of Tests=3-9, as BM-37 is a calcite form, while the others are acicular aragonite form.
N.A. - Not available.

Notes:

1. The determination of a specific gravity (S.G.) of particulate precipitated aragonite calcium carbonate of the present invention, in a range below 2.5 g/cm³ (after drying at 120°C for twelve hours as described above, as well as after ignition of the dried material at 500°C for eight hours) is actually an

important and decisive test to consider if the technology that was used is under the domain of the present invention.

2. Only the inclusion of gas (probably, as tiny bubbles or "blisters") in closed pores can account for the dramatic reduction of the S.G. of particulate precipitated aragonite calcium carbonate of the present invention. The L.O.D. and the L.O.I. in the latter tests (c. f. (B) and (C), respectively) do not leave many logical choices to account for this phenomenon. Also, this is in accordance with the facts I. that the product of the present invention is obtained under flotation conditions, and II. that the high hiding power of the paints, in which the particulate precipitated aragonite calcium carbonate of the present invention was used, are probably due to the high effective refractive index of this product of the present invention, which is much higher than that expected of similar products that are produced according to the prior art (c. f. data collected in EXAMPLE 15 and the comparison made to paint formulations that were based on raw materials of the prior art).

3. The idea of using porous particles, to increase their effective refractive index in coatings, is not new. For instance, Rohm & Haas produces a series of such products, e. g. Ropaque® OP96 and Ropaque® OP3000. However, these particles are of an organic polymeric nature of which cost and adaptation to the environment is not to be compared with precipitated calcium carbonate particles.

(B) Determination of the Specific Gravity (S.G.) in Tall Oil of a Product Calcined at 300°C

1. The wet filter cake of the $CaCO_3$ sample was dried for 12 hours at 120°C to remove all the free water.

2. The weighed dry sample was heated for 8 hours at 300°C. The loss on drying (L.O.D.) was then determined.

3. The S.G. of the heated powder was measured as above (c. f. (A)).

4. The loose bulk density (B.D.) of the dry powder was measured using a balance and a graduated cylinder.

The results are as follows:

Table 14- the results of EXAMPLE 14 (B)

Test #	Sample Code	Active agent	Dosage (wt.%)	L.O.D. wt.% 300°C	S.G.† g/cm³	Loose B.D.† g/cm³
10	Natural $CaCO_3$	-	-	0.10	2.63	0.651
11	BM-37*	decanoic acid	1	2.21	2.64	0.372
12	C**	N.A.	N.A.	1.3	2.63	0.54
13	AR-81	decanoic acid	0.5	0.83	2.19	0.255
14	AR-83	decanoic	1	0.89	2.11	0.265

		acid				
15	AR-118	decanoic acid	2	2.32	2.03	0.200
16	AR-119	decanoic acid	5	5.73	2.01	0.200
17	AR-135	nonanoic acid	1	0.95	2.12	0.238
18	AR-120	decanoic acid	2^	2.27	2.02	0.235

* - The sample was taken from the batch mode of operation in-EXAMPLE 3.
** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.
^ - 50ppm of phosphoric acid were used in addition to the decanoic acid.
† - A dry powder after heating for 8 hours at 300°C.
N.A. - Not available.

(C) Determination of the Specific Gravity (S.G.) in Tall Oil of a Product Calcined at 500°C

1. The wet filter cake of the $CaCO_3$ sample was dried for 12 hours at 120°C to remove all the free water.

2. The dry sample was calcined for 8 hours at 500°C. The loss on ignition (L.O.I.) was then determined.

3. The S.G. of the calcined powder was measured as above.

4. The loose bulk density (B.D.) of the dry powder was measured using a balance and a graduated cylinder.

The results are as follows:

Table 15 - the results of EXAMPLE 14 (C)

Test #	Sample Code	Dosage %(wt)	L.O.I. %(wt) 500°C^^	S.G.† g/cm³	Loose B.D.† g/cm³
19	Natural $CaCO_3$	-	0.18	2.70	0.75
20	BM-37	1*	2.58	2.60	0.38
21	C**	N.A.	2.02	2.71	0.55
22	AR-81	0.5	1.32	2.13	0.23
23	AR-83	1	1.44	2.03	0.22
24	AR-118	2	2.07	2.01	0.18
25	AR-119	5***	5.25	1.93	0.19
26	AR-135	1	1.44	2.01	0.24
27	AR-120	2^	2.37	1.91	0.18

* - The sample was taken from the batch mode of operation in -EXAMPLE 3.
** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.

*** - 5g of AR-119 were dissolved in a 10% HCl solution. No decanoic acid could be extracted or detected, as is expected of such molecules when they are subjected to heating for 8 hours at 500°C.
^ - 50ppm of phosphoric acid were used in addition to the decanoic acid.
^^ - Aragonite is converted into calcite at T > 400°C.
† - Table 13 - the results of EXAMPLE 14 (A)hours at 500°C.
N.A. - Not available.

(D) Determination of the Specific Gravity (S.G.) - by a Gas Pycnometer

$CaCO_3$ powder (d_{50}=3.5 microns) of Polychrom, Israel - "Girulite-8" and AR-118, a product of the present invention, were tested in a AccPyc 1330 ex Micromeritics – USA. The results are given in Table 15a, as follows:

Table 15a - the results of EXAMPLE 14 (D):

Sample Code	Test #	S. G. (g/cm^3)	Average S. G. (g/cm^3)
G-8	1	2.7544	2.7538
	2	2.7549	
	3	2.7547	
	4	2.7529	
	5	2.7523	
AR-118	1	2.9070	2.8903*
	2	2.8918	
	3	2.8932	
	4	2.8848	
	5	2.8750	

* - This experiment demonstrates that: (I) the product of the present invention is permeable to air (especially under vacuum and pressure) and (II) the product of the present invention would not have been discovered had this routine technique used to determine the S. G. of the products of the present invention and even those skilled in the art could overlook the whole phenomenon of "porous" PCC, which is the basis of this invention.

(E) Determination of the Specific Gravity (S.G.) of a Product Calcined at 500°C - In a Water Pycnometer

It seems that the practice described in EXAMPLE 14 (A) and 14 (C) of determining the specific gravity (S. G.) of the PCC of the present invention in tall oil, is quite tedious and it may lead to mistakes, especially due to the adhering bubbles to hydrophobic surfaces of the PCC particles, and also as a result of using excessive sonication energies, which may cause the penetration of the tall oil into the "pores" in the product of the present invention. Therefore, it is recommended to use a simple and more accurate test to distinguish between a

product (process) of the present invention and a product (process) of the prior art. The test is based on the fact that the product of the present art, after calcining it at 500°C for eight hours, looses the hydrophobic compounds, but the "pores" that have been created in the PCC particles during the process of the present invention, do (can) not disappear. Once the hydrophobic nature of the particles have been "eliminated", pure water can easily wet the surface of these particles, and even to penetrate somewhat into "pores" that are close to the surface. For this test, a skilled person in the art does not need any sonication, but rather a gentle mixing for 5 mins. of the slurry of pure water (e.g. HPLC grade) and the calcined PCC at 500°C for eight hours, using a laboratory magnetic stirrer. Beyond that the steps of such an analysis are very similar to those described in EXAMPLE 14 (A) – steps 1-5, as follows:

1. The wet filter cake of the $CaCO_3$ sample should be calcined for eight hours at 500°C to remove all water and organic molecules (the sample can be dried first at 120°C for twelve hours. However, this option may be considered a G.M.P., but it is not all mandatory).
2. A weighed quantity of the calcined $CaCO_3$ sample (Wc) (at about ambient temperature) + a weighed quantity of pure water (Ww) (of a density that is practically 1.0 g/cm^3) are introduced into a 1 l. glass pycnometer (a 100ml, 250 ml or 500ml pycnometers can also be used, depending on the accuracy of the lab. balance).
3. The mixture is stirred with a laboratory magnetic stirrer for exactly 5 minutes.
4. The magnet is "fished-out"; and more pure water is added to fill the pycnometer to the desire volume.
5. The pycnometer bottle is then evaluated at 21°C±1°C for:

(a) the volume of the slurry - V

(b) the total net weight of the slurry - W

Based on the above measurements, the following was calculated:

(1) from the equation: D = W/V g/cm^3, the density of the slurry;

(2) from the equation

1/D = [Wc(Ww + Wc)]/S.G. + [Ww(Ww+Wc)]/1.0,

the S.G. of the $CaCO_3$ sample was calculated.

The results are as follows:

Table 15b - the results of EXAMPLE 14 (E)

Test #	Sample Code	Active agent	CO_2 (%)	Dosage (wt%)	S.G. 500°C in Water (g/cm^3)
28	Natural CaCO3	-	-	-	2.71
29	GCC-8[1]	-	-	-	2.73
30	GCC-8[2]	Decanoic A.	N.A.	2.0	2.63
31	PCC[3]	N.A.	N.A.	N.A.	2.75
32	PCC[4]	Decanoic A.	N.A.	2.0	2.69
33	OM-95[A]	-	-	-	2.63
34	UPCC[B]	N.A.	N.A.	N.A.	2.63
35	BM-37	Decanoic A.	100.0	1*	2.67
36	AR-81	Decanoic A.	100.0	0.5	2.41
37	AR-83	Decanoic A.	100.0	1	2.33
38	AR-118	Decanoic A.	100.0	2	2.21
39	AR-119	Decanoic A.	100.0	5**	2.16
40	AR-135	Decanoic A.	100.0	1	2.35
41	AR-120	Decanoic A.	100.0	2***	2.19
42	ARP-35	Decanoic A.	26.0	1.5	2.26
43	ARP-36	Decanoic A.	26.0	2.0	2.02
44	ARP-61	Decanoic A.	100.0	2.0	1.98
45	ARP-62-1	Decanoic A.	100.0	3.0	2.01
46	ARP-51	Lauric A.	26.0	1.5	2.15
47	ARP-65	Lauric A.	50.0	1.5	2.30
48	ARP-76	Undecylenic A.	50.0	1.5	2.24
49	ARP-77	Myristic A.	50.0	1.5	2.36
50	ARP-70	Stearic A.	50.0	1.5	2.18
51	ARP-71	Isostearic A.	50.0	1.5	2.63
52	ARP-72	Oleic A.	50.0	1.5	2.70
53	ARP-83	Palmitic A.	50.0	1.5	2.61

* - The sample was taken from the batch mode of operation in -EXAMPLE 3 is quite pure calcite)

** - 5g of AR-119 were dissolved in a 10% HCl solution. No decanoic acid could be extracted or detected, as is expected of such molecules when they are subjected to heating for 8 hours at 500°C.

*** - 50ppm of phosphoric acid were used in addition to the decanoic acid.

[1] -"Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom – Israel.

[2] – "Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom - Israel, which was coated using 2 wt% n-decanoic acid.

[3] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.

[4] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40, which was coated using 2 wt% n-decanoic acid.

[5] - 50ppm of phosphoric acid were used in addition to the decanoic acid.

[A] – Commercial ultrafine stearic acid coated - UFT 95 GCC natural calcite (95 wt% pass 2μ size) ex Omya-Pluess-Staufer - Switzerland.
[B] – Commercial ultrafine stearic acid coated - Ultraflex PCC calcite ex SMI - USA.
N.A. - Not Available.

(F) The Final Determination of the Specific Gravity (S.G.) of a Product Calcined at 500°C

In most practical instances the use of EXAMPLE 14 (A) and EXAMPLE 14 (C) or the use of only EXAMPLE 14 (E) to determine the specific gravity of the PCC products, may not cause any dispute and a person skilled in the art can observe quite easily that the product of the present invention is quite different from the product of the prior art, by just observing the considerable differences between the loose bulk density (L.B.D.) of the aragonite particles of the present invention compared to those of the aragonite particles of the prior art. (Table 13, 14, and 15). However, when the specific gravity (S. G.) of the PCC particles, in question, is quite close to 2.5 g/cm^3, the accuracy of the analytical method may be of prime importance. As it seems now, the determination of the specific gravity of the PCC particles that were calcined first is quite accurate, and that this procedure according EXAMPLE 14 (E) is also quite simpler and faster. Therefore, the determination of the S.G. values should be conducted as follows:

(a) The specific gravity (S.G.) determination should be conducted according to. EXAMPLE 14 (A) and EXAMPLE 14 (C), and separately, according to ii. EXAMPLE 14 (E), (independently of the results in i.).

(b) The lowest of the S.G. results obtained for a certain product in (a), according to EXAMPLE 14 (C) and according to EXAMPLE 14 (E), independently, will determine whether the product (and the process) is in the domain of the present invention (namely, S.G. <2.5 g/cm^3).

(G) Determination of the Loose Bulk Density (L.B.D.) of a Product Dried at 120°C

The L.B.D. of a dry sample (at 120°C for twelve hours) was determined, separately and independently of the S.G. analyses, according to the ASTM D1895, as follows. A sample is de-agglomerated gently in a mortar/pestle and sieved through a 0.6 mm screen. The fine powder that passes the screen is introduced into a 250 ml plastic graduate cylinder, which is then mounted on a screen-shaker (Rotap Model RX-29-10 ex W.S. Tyler Inc. – USA), the apparatus being then operated for exactly 5 minutes. This test is repeated three

times for each sample, the reported L.B.D. being the average of these tests. The results are reported already in Table 13 (above) and in Table 15c as follows:

Table 15c - the results of EXAMPLE 14 (G)

Test #	Sample Code	Active agent	CO_2 (%)	Dosage (wt%)	L.B.D. 120°C (g/cm³)	L.B.D. 500°C (g/cm³)
54	Natural $CaCO_3$	-	-	-	0.65	0.75
55	GCC-8[1]	-	-	-	0.65	0.56
56	GCC-8[2]	Decanoic A.	N.A.	2.0	0.64	0.56
57	PCC[3]	N.A.	N.A.	N.A.	0.71	0.55
58	PCC[4]	Decanoic A.	N.A.	2.0	0.70	0.53
59	OM-95[A]	-	-	-	0.66	0.49
60	UPCC[B]	N.A.	N.A.	N.A.	0.50	0.37
61	BM-37	Decanoic A.	100.0	1*	0.37[BM]	0.38
62	AR-81	Decanoic A.	100.0	0.5	0.31	0.23
63	AR-83	Decanoic A.	100.0	1	0.30	0.22
64	AR-118	Decanoic A.	100.0	2	0.25	0.18
65	AR-119	Decanoic A.	100.0	5**	0.29	0.19
66	AR-135	Decanoic A.	100.0	1	0.31	0.24
67	AR-120	Decanoic A.	100.0	2***	0.23	0.18
68	ARP-35	Decanoic A.	26.0	1.5	0.33	0.18
69	ARP-36	Decanoic A.	26.0	2.0	0.33	0.20
70	ARP-61	Decanoic A.	100.0	2.0	0.38	0.25
71	ARP-62-1	Decanoic A.	100.0	3.0	0.31	0.28
72	ARP-51	Lauric A.	26.0	1.5	0.31	0.17
73	ARP-65	Lauric A.	50.0	1.5	0.38	0.21
74	ARP-76[5]	Undecylenic A.	50.0	1.5	0.38	0.18
75	ARP-77	Myristic A.	50.0	1.5	0.37	0.18
76	ARP-70[7]	Stearic A.	50.0	1.5	0.37	0.19
77	ARP-71	Isostearic A.	50.0	1.5	0.69	0.53
78	ARP-72	Oleic A.	50.0	1.5	0.70	0.53
79	ARP-83	Palmitic A.	50.0	1.5	0.86	0.54

* - The sample was taken from the batch mode of operation in - EXAMPLE 3 is quite pure calcite)

** - 5g of AR-119 were dissolved in a 10% HCl solution. No decanoic acid could be extracted or detected, as is expected of such molecules when they are subjected to heating for 8 hours at 500°C.

*** - 50ppm of phosphoric acid were used in addition to the decanoic acid.

[1] -"Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom – Israel.

[2] – "Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom - Israel, which was coated using 2 wt% n-decanoic acid.

[3] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.

[4] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40, which was coated using 2 wt% n-decanoic acid.
[5] - 50ppm of phosphoric acid were used in addition to the decanoic acid.
[6] -The XRD spectrum and SEM of ARP-76 are presented in Fig.6 and Fig. 7, respectively.
[7] -The XRD spectrum and SEM of ARP-70 are presented in Fig.8 and Fig. 9, respectively.
[A] Commercial ultrafine stearic acid coated - UFT 95 GCC natural calcite (95 wt% pass 2μ size) ex Omya-Pluess-Staufer - Switzerland.
[B] – Commercial ultrafine stearic acid coated - Ultraflex PCC calcite ex SMI - USA.
[BM] – The product of the batch mode operation is a calcite PCC.
N.A. - Not Available.

The results in Tables 13 and in Table 15c represent the products of the present invention if they have a L.B.D. <0.4 g/cm^3. However, those results count, if the GSA (BET) of the specific samples in test are <13 m^2/g. Those samples that do not meet this requirement, can only be tested according to EXAMPLE 14 (F).

Note:
It is worthwhile to observe the dramatic L.B.D. changes that occur when the products of the present invention are subjected to high temperature treatment (at 300°C and especially at 500°C), which is probably due to the thermal collapse of the "porous" structure of these particles.

(H) Determination of the Specific Gravity (S.G.) in Oils of Products Dried at 120°C

The specific gravity of various calcium carbonate particles was measured in various oils, as described in Example 14 (A). The results indicate that the low S.G. values is not due to the tall oil that we used, but it is rather common to many similar liquids. In cases at which the S.G. values are close to 2.5 g/cm^3, the well-defined oleic acid (of purity > 97%) can be used to resolve any dispute, and in any case, the instructions in EXAMPLE 14 (F) and EXAMPLE 14 (G), still prevail.

The process set points - continuous mode of operation:

1. Rotor Speed = 2500 rpm (Rotor Diameter = 8.5 cm)
2. pH = 9.5±0.2
3. Temperature = 85°C±3
4. Carbon dioxide flow rate = 2 m^3/hr.
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 50-70 L.P.H. (to maintain the preset pH value).

6. Active agent concentration = decanoic acid; 0 - 2 wt.% based on $CaCO_3$.

7. Reactor Volume=30 l. (Diameter=8.7cm).

The results are:

Table 15d - the results of EXAMPLE 14 (H):

Test #	Sample Code	Active Agent	Dosage (wt%)	CO_2 (%)	Liquid[6,7] in Pycnometer	S.G.[7] g/cm^3 120°C
80	GCC-8[1]	-	-	-	Sylvatal 20S	2.63
81	PCC[3]	-	-	N.A.	Sylvatal 20S	2.56
82	GCC-8[2]	Decanoic A.	2.0	-	Sylvatal 20S	2.23
83	PCC[4]	Decanoic A.	2.0	N.A.	Sylvatal 20S	2.31
84	AR-118[5]	Decanoic A.	2.0	100.0	Sylvatal 20S	1.77
85	AR-118[5]	Decanoic A.	2.0	100.0	Sylvatal-20S	1.75
86	AR-118[5]	Decanoic A.	2.0	100.0	Oleic (>97%)	1.79
87	ARP-29	Decanoic A.	0.7	26.0	Sylvatal 20S	1.98
88	ARP-31	Decanoic A.	1.0	26.0	Sylvatal 20S	1.85
89	ARP-35	Decanoic A.	1.5	26.0	Sylvatal 20S	1.57
90	ARP-35	Decanoic A.	1.5	26.0	Oleic (>97%)	1.64
91	ARP-35	Decanoic A.	1.5	26.0	Oleic (>97%)	1.62
92	ARP-35	Decanoic A.	1.5	26.0	Canola Oil	1.66
93	ARP-35	Decanoic A.	1.5	26.0	Soybean Oil	1.60
94	ARP-35	Decanoic A.	1.5	26.0	Sunflower Oil	1.58
95	ARP-35	Decanoic A.	1.5	26.0	Corn Oil	1.61
96	ARP-35	Decanoic A.	1.5	26.0	Mazola Oil	1.59
97	ARP-35	Decanoic A.	1.5	26.0	Olive Oil	1.63
98	ARP-36	Decanoic A.	2.0	26.0	Sylvatal 20S	1.34
99	ARP-36	Decanoic A.	2.0	26.0	Sylvatal-20S	1.35
100	ARP-36	Decanoic A.	2.0	26.0	Oleic (>97%)	1.36
101	ARP-37	Decanoic A.	2.0	15.0	Sylvatal 20S	1.28
102	ARP-51	Lauric A.	1.5	26.0	Sylvatal 20S	1.78
103	ARP-61	Decanoic A.	2.0	100.0	-	-
104	ARP-62-1	Decanoic A.	3.0	100.0	-	-
105	ARP-65	Lauric A.	1.5	50.	Sylvatal 20S	2.04
106	ARP-70	Stearic A.	1.5	50	Sylvatal 20S	2.36
108	ARP-71	Isostearic A.	1.5	50	Sylvatal 20S	2.71
109	ARP-72	Oleic A.	1.5	50	Sylvatal 20S	2.58
110	ARP-76	Undecylenic A.	1.5	50	Sylvatal 20S	2.02
111	ARP-77	Myristic A.	1.5	50	Sylvatal 20S	2.15
112	ARP-77/1	Palmitic A.	1.5	50	Sylvatal 20S	2.61

113	ARP-78	Linoleic A.	1.5	50	Sylvatal 20S	2.59

[1] - "Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom – Israel.
[2] – "Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom - Israel, which was coated using 2 wt% n-decanoic acid.
[3] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.
[4] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40, which was coated using 2 wt% n-decanoic acid.
[5] – AR-118, a product of the present invention, mentioned already in EXAMPLE 14 (A), above.
[6] – The specific gravity of the liquids were as follows: Oleic A.=0.887 g/cm^3; Tall Oil (Sylvatal 20S ex Arizona Chemical - USA)=0.930 g/cm^3; Refined Canola Oil (ex Milumor – Israel)=0.910 g/cm^3; Refined Corn Oil (ex Milumor – Israel)=0.910 g/cm^3; Refined Corn Oil (Mazola ex Bestfoods – USA)=0.915 g/cm^3; Refined Soybean Oil (ex Milumor – Israel)=0.920 g/cm^3; Refined Sunflower Oil (ex Milumor – Israel)=0.918 g/cm^3; Cold Pressed olive Oil (ex Shemen Industries – Israel)=0.893 g/cm^3
[7] – The S.G. analyses were conducted at 21°C±1°C.
N.A. – Not available

EXAMPLE 15 - Preparation of Exterior White Paint - Hercules Inc.

The procedure for the preparation of this paint was obtained from Hercules Inc.; Cellulose & Protein Products D.; Wilmington, DE 19899 (USA). The procedure followed quite closely the Celanese Resins Formulation No. EP-48-222 for the production of this Exterior White Paint (Vinyl Acetate & Acrylate).

(A) The ingredients used for the 52% PVC Paint and their function are as follows:

1. Tap water.
2. Nopco NDW defoamer.
3. Cellosize QP 15000 thickener (hydroxy ethyl cellulose).
4. Disperse One (45% N.V.) (dispersant).
5. Synperonic NP10 surfact; wetting agent.
6. Kronos 2160 TiO_2 pigment.
7. Synthetic sodium aluminum silicate (p820) (spacer).
8. Kaolin clay (D_{50} = 3.1 micron)(spacer).
9. $CaCO_3$ (spacer) - A GCC product of Polichrom Ltd., Israel.
10. Talc (D_{50}=12.3 micron)(spacer).
11. PCC - Aragonite of the present invention (samples used contained >80% $CaCO_3$ in the wet cake products before their drying; no diminution operation

took place prior to this use. Namely, the PCC - Aragonite used is not necessarily yet optimized for its purpose).

12. Copolymer vinyl acetate acrylate (55% N.V.) (emulsion).
13. Butyl diglycol acetate solvent (coalescent agent).
14. Kathon LXE preservative.
15. 25% Ammonia (base).
16. Tap water.

Tap water (1), defoamer (2) and thickener (3) were added to a plastic container (d=20 cm; h=30 cm) equipped with a disk (d=8 cm) attached to a Dissolver (Homo Dispers Model HD-550 (0.75 HP) of Hslangtai Machinery Industry Co. Ltd.; Taiwan). The mixture was stirred at 500 rpm for 5 minutes, after which the dispersant (4) and the wetting agent (5) were added, and stirring was continued at 500 rpm for additional 5 minutes. At this point the stirring speed was increased to 1500 rpm and the respective ingredients for the respective formulations 1- 10 were added consecutively, each ingredient over a 5 minute period, according to the order in the above list of reagents (6 - 16).

The physical properties of the above paints were measured, including the most important property - the hiding power (%) of 90 μm layers of paint were determined with an ACS instrument (Applied Color Systems) and the results are given in the following Tables 19 and 20:

Table 19 - the results of EXAMPLE 15

Exterior White Paint - Hercules Inc. Evaluation of the 52% PVC Paints Based on the Precipitated Aragonite Calcium Carbonate Particles of the Present Invention (PCC - Aragonite)						
Raw Material	1	2	3	4	5	6
	% (wt)					
Tap Water	25.0	25.0	25.0	25.0	25.0	25.0
Defoamer	0.1	0.1	0.1	0.1	0.1	0.1
Thickener(15K)	0.3	0.3	0.3	0.3	0.3	0.3
Dispersant (45%)	0.9	0.9	0.9	0.9	0.9	0.9
Wetting Agent	0.35	0.35	0.35	0.35	0.35	0.35
TiO_2; Kronos	14.0	9.0	9.0	9.0	9.0	8.4
Silicate	3.7	3.7	3.7	3.7	4.0	3.9
$CaCO_3$ - GCC	7.0	-	-	-	-	-
Kaolin Clay	6.5	6.5	6.5	6.5	10.7	6.8
Talc	6.3	-	-	-	-	-
PCC-Aragonite*	-	17.75	17.75	17.75	13.00	17.75
Copolymer (55%)	24.5	25.5	25.5	25.5	25.4	25.4
Coalescent Agent	0.1	0.1	0.1	0.1	0.1	0.1
Preservative	0.5	0.5	0.5	0.5	0.5	0.5
Ammonia	0.3	0.3	0.3	0.3	0.3	0.3
Tap Water	10.45	10.0	10.0	10.0	10.35	10.2
Total	100.	100.	100.	100.	100.	100.
The Characteristics of the Paint						
Solids (%)	50.98	50.98	50.98	50.98	50.67	50.82
P.V.C. (%)	51.77	51.32	51.32	51.32	51.51	51.55
Hiding Power (%)	94.0	94.4	94.9	95.5	95.1	94.9
Viscosity (K.U.)	92.0	92.0	93.2	98.0	100.0	98.0
Hegman	4.5	5.5	5.5	5.0	4.0	4.5
Bulk Density	1.317	1.259	1.257	1.248	1.226	1.221
Saving of TiO_2 (%)	-	35.7	35.7	35.7	35.7	40.0
Weight Saving (%)	-	4.4	4.6	5.2	6.9	7.3

Formulation No.	Pigment*	Sample Code	Active Agent	Active Agent % (wt)
1	Reference Paint	-	-	-
2	PCC - Aragonite	AR-81	Decanoic	0.5
3	PCC - Aragonite	AR-83	Decanoic	1.0
4	PCC - Aragonite	AR-118	Decanoic	2.0
5	PCC - Aragonite	AR-119	Decanoic	5.0
6	PCC - Aragonite	AR-118	Decanoic	2.0

Table 20 - the results of EXAMPLE 15

Exterior White Paint - Hercules Inc. Evaluation of the 52% PVC Paints Based on the Precipitated Aragonite Calcium Carbonate Particles of the Present Invention (PCC - Aragonite)						
Raw Material	**1**	**7**	**8**	**9**	**10**	
	% (wt)					
Tap Water	25.0	25.0	25.0	25.0	25.0	
Defoamer	0.1	0.1	0.1	0.1	0.1	
Thickener(15K)	0.3	0.3	0.3	0.3	0.3	
Dispersant (45%)	0.9	0.9	0.9	0.9	0.9	
Wetting Agent	0.35	0.35	0.35	0.35	0.35	
TiO_2; Kronos	14.0	7.0	7.0	6.3	12.0	
Silicate	3.7	4.8	4.2	4.2	3.7	
$CaCO_3$ - GCC	7.0	-	-	-	-	
Kaolin Clay	6.5	7.1	12.5	13.1	6.5	
Talc	6.3	-	-	-	-	
PCC-Aragonite*	-	17.75	13.0	13.0	15.3*	
Copolymer (55%)	24.5	25.5	26.0	26.0	24.5	
Coalescent Agent	0.1	0.1	0.1	0.1	0.1	
Preservative	0.5	0.5	0.5	0.5	0.5	
Ammonia	0.3	0.3	0.3	0.3	0.3	
Tap Water	10.45	10.3	9.75	9.85	10.45	
Total	100.	100.	100.	100.	100.	
The Characteristics of the Paint						
Solids (%)	50.98	50.98	50.98	50.98	50.98	
P.V.C. (%)	51.77	51.32	51.32	51.32	51.91	
Hiding Power (%)	94.0	94.2	94.3	94.0	92.7	
Viscosity (K.U.)	92.0	96.8	98.8	98.0	90.2	
Hegman	4.5	4.5	4.5	4.5	4.5	
Bulk Density	1.317	1.179	1.159	1.224	1.300	
Saving of TiO_2 (%)	-	50.0	50.0	55.0	14.3	
Weight Saving (%)	-	10.5	12.0	7.0	1.3	

Formulation No.	Pigment*	Sample Code	Active Agent	Active Agent % (wt)
1	Reference Paint	-	-	-
7	PCC - Aragonite	AR-118	Decanoic	2.0
8	PCC - Aragonite	AR-119	Decanoic	5.0
9	PCC - Aragonite	AR-119	Decanoic	5.0
10	PCC - Aragonite	C**	N.A.	N.A.

** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.

(B) <u>The ingredients of the 32% PVC Paint and their function are as follows:</u>

1. Tap water.
2. Nopco NDW defoamer.
3. Cellosize QP 15000 thickener (hydroxy ethyl cellulose).
4. Disperse One (45% N.V.) (dispersant).
5. Synperonic NP10 surfactant; wetting agent.
6. Kronos 2160 TiO_2 pigment. 7.
7. Synthetic Na-Al silicate (p820) (spacer).
8. Kaolin clay (D_{50} = 3.1 micron)(spacer)
9. $CaCO_3$ (spacer) - a GCC product of Polichrom Ltd., Israel
10. Talc ($\widehat{D}_{50}$=12.3 micron)(spacer)
11. PCC - aragonite of the present invention (samples used contained >80% $CaCO_3$ in the wet cake products before their drying; no diminution operation took place prior to this use. However, the PCC - aragonite used is not necessarily yet optimized for its purpose).
12. Propylene glycol (solvent).
13. Copolymer vinyl acetate acrylate (55% N.V.) (emulsion).
14. Butyl diglycol acetate solvent (coalescent agent).
15. Kathon LXE preservative.
16. 25% Ammonia (base).
17. Tap water.

Tap water (1), defoamer (2) and thickener (3) were added to a plastic container (d=20 cm; h=30 cm) equipped with a disk (d=8 cm) attached to a Dissolver (Homo Dispers Model HD-550 (0.75 HP) of Helangtai Machinery Industry Co. Ltd.; Taiwan). The mixture was stirred at 500 rpm for 5 minutes, after which the dispersant (4) and the wetting agent (5) were added, and stirring was continued at 500 rpm for additional 5 minutes. At this point the stirring speed was increased to 1500 rpm and the respective ingredients for the respective formulations 1- 10 were added consecutively, each ingredient over a 5 minute period, according to the order in the above list of reagents (6 - 15).

The physical properties of the above paints were measured, including the most important property - the hiding power (%) of 90 μm layers of paint were

determined with an ACS Instrument (Applied Color Systems) and the results are given in the following Table 21:

Table 21 - the results of EXAMPLE 15

Exterior White Paint - Hercules Inc. Evaluation of the 32% PVC Paints Based on the Precipitated Aragonite Calcium Carbonate Particles of the Present Invention (PCC - Aragonite)						
Raw Material	11	12	13	14	15	16
	% (wt)					
Tap Water	17.8	17.8	17.8	17.8	17.8	17.8
Defoamer	0.15	0.15	0.15	0.15	0.15	0.15
Thickener(15K)	0.22	0.22	0.22	0.22	0.22	0.22
Dispersant (45%)	0.60	0.60	0.60	0.60	0.60	0.60
Wetting Agent	0.34	0.34	0.34	0.34	0.34	0.34
TiO_2; Kronos	22.5	20.0	20.0	19.0	18.0	19.0
Silicate	2.25	2.25	2.25	2.25	2.25	-
CaCO3 - GCC	5.0	-	-	-	-	-
PCC-Aragonite*	-	7.5	7.5	8.5	9.25	13.0
Propylene Glycol	2.70	2.70	2.70	2.70	2.70	2.70
Copolymer (55%)	37.45	37.45	37.45	37.45	38.0	33.4
Coalescent Agent	0.18	0.18	0.18	0.18	0.18	0.18
Preservative	0.45	0.45	0.45	0.45	0.45	0.45
Ammonia	0.30	0.30	0.30	0.30	0.30	0.30
Tap Water	10.06	10.06	10.06	10.06	9.76	11.86
Total	100.	100.	100.	100.	100.	100.
The Characteristics of the Paint						
Solids (%)	50.35	50.35	50.35	50.35	50.35	50.37
P.V.C. (%)	32.59	32.64	32.64	32.93	32.64	36.73
Hiding Power (%)	91.0	91.4	91.4	91.0	90.8	91.0
Viscosity (K.U.)	87.2	98.0	97.4	96.2	87.8	90.2
Hegman	5.5	5.5	5.5	5.5	5.0	5.5
Bulk Density	1.18	1.128	1.127	1.109	1.005	1.073
Saving of TiO_2 (%)	-	11.1	11.1	15.5	20.0	15.5
Weight Saving (%)	-	4.4	4.5	6.0	14.8	6.8

Formulation No.	Pigment*	Sample Code	Active Agent	Active Agent % (wt)
11	Reference Paint	-	-	-
12	PCC - Aragonite	AR-118	Decanoic	2.0
13	PCC - Aragonite	AR-119	Decanoic	5.0
14	PCC - Aragonite	AR-119	Decanoic	5.0
15	PCC - Aragonite	AR-119	Decanoic	5.0
16	PCC - Aragonite	AR-118	Decanoic	2.0

Notes:

1. The particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite) can be used to produce paints without a substantial prior size reduction, except that effected by the mixing system of the production of the paint, which is anyway being used in this art to thoroughly disperse the pigments in the various formulations.

2. Though the particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite) is not yet optimized for its use in the production of paints and though the formulations used are by no means optimized, still this product is able to substitute over 50% of the expensive titanium oxide pigment without any deterioration of the resulting paint, as it manifested by the hiding power measured.

3. As the coatings (paints) are being sold and used by volume, and not by weight, the additional saving resulting from using the particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite) can surpass 10% on all the constituents of the coating, including the titanium oxide.

4. For simplicity in formulating the above mentioned paints, dry samples of The particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite), were used. However, wet filter cakes that contain even more water than 20% wt.%, based on wet $CaCO_3$ cake, can be used, provided that this water is being taken in account. However, on an industrial scale, dry PCC-Aragonite will be rarely used, due to the economy of using the wet product.

(C) A Comparison of Modified Paint formulations Containing Various GCC/PCC

The experimental of EXAMPLE 15 (A) was repeated, except that the paint compositions contained only one selected PCC/GCC pigment (>50 wt%) at a time and the minimum required ingredients that were necessary to prepare these basic modified paint formulations. A standard (STD) interior paint formulation was used as a general reference.

The paint compositions are as follows:

Table 22 – STD vs. Modified paint formulation of EXAMPLE 15 (C)

Raw Material	S T D	Modified
Water	28.25	28.87
Defoamer	0.30	0.38
Thickener	0.20	0.09
Dispersant	0.40	0.00
Wetting Agent	0.30	0.00
TiO_2	7.5	0.00
Silicate	3.5	0.00
Talc	13.0	0.00
G.C.C.	34.0	0.00
AR-pigment	0.00	57.28
Propylene glycol	1.00	0.56
Copolymer – 50% solids	11.40	12.72
Biocide	0.15	0.10
T o t a l	**100.0**	**100.0**
% Solids in paint	63.7	64.3

The physical and optical properties of the pigments used and the paint obtained are reported as follows:

Table 23 – the pigments properties in EXAMPLE 15 (C)

Paint	Pigment Code	Active Agent	Dosage (wt%)[3]	CO_2 (v%(	S.S.A. (BET) (m^2/g)	PSD[4] μ	
						D_{50}	D_{80}
STD	-	-	-	-	-	-	-
1	PCC[1]	-	-	-	12.0	2.0	0.8
2	GCC[2]	-	-	-	4.0	5.0	2.1
3	ARP-29	Decanoic A.	0.7	26.0	5.7	4.49	1.98
4	ARP-31	Decanoic A.	1.0	26.0	6.2	3.54	1.68
5	ARP-34	Decanoic A.	1.5	100	11.1	2.68	1.27
6	ARP-35	Decanoic A.	1.5	26.0	11.5	3.0	1.65
7	ARP-36	Decanoic A.	2.0	26.0	15.4	2.51	0.73
8	ARP-37	Decanoic A.	2.0	15.0	10.9	2.20	0.93
9	ARP-51	Lauric A.	1.5	26.0		4.14	2.39
10	ARP-61	Decanoic A.	2.0	100	15.5	1.8	0.68
11	APR-65	Lauric A.	1.5	50.0	8.2	5.4	3.1
12	ARP-70	Stearic A.	1.5	50.0	4.3	5.3	1.6
13	ARP-71	Isostearic	1.5	50.0	1.9	9.3	5.9
14	ARP-72	Oleic A.	1.5	50.0	3.7	10.9	6.5
15	ARP-76	Undecylenic A.	1.5	50.0	13.1	2.7	1.5
16	ARP-77	Myristic A.	1.5	50.0	5.2	3.8	2.3
17	ARP-83	Palmitic A.	1.5	50.0			

[1] - Commercial stable PCC Slurry of Aragonite (Opacarb® A40 ex SMI – USA). Calculation of the S.G. of the aragonite particles in a 69.6% commercial slurry resulted in 2.83 g/cm^3. Naturally, this slurry was used to produce the paint above.

[2] - CaCO3 (spacer) - a GCC (Calcite ex Polichrom Ltd. – Israel).

[3] – Calculated as the acid form, based on the CaCO3.
[4] – The PCC of the present invention has not undergone any size reduction prior to its use, except the size reduction that may happen during regular operations.

Table 24 – the paint properties in EXAMPLE 15 (C)

Paint Code	Pigment Code	Active Agent	Dosage (wt%)[3]	CO_2 (v%(	S.G.[4] 500°C Water (g/m^3)	Paint	
						Gloss[5]	Hiding[6] Power
STD	-	-	-	-	-	2.1	83.7
1	PCC	-	-	-	2.69[1]	31.9	88.0
2	GCC[2]	-	-	-	2.62	2.2	80.9
3	ARP-29	Decanoic A.	0.7	26.0	2.32	3.0	92.6
4	ARP-31	Decanoic A.	1.0	26.0	2.29	3.6	96.5
5	ARP-34	Decanoic A.	1.5	100	2.38	7.5	96.3
6	ARP-35	Decanoic A.	1.5	26.0	2.26	4.0	99.8
7	ARP-36	Decanoic A.	2.0	26.0	2.02	5.5	98.1
8	ARP-37	Decanoic A.	2.0	15.0	1.90	5.2	99.5
9	ARP-51	Lauric A.	1.5	26.0	2.15	4.3	94.8
10	ARP-61	Decanoic A.	2.0	100	1.98	11.5	98.3
11	APR-65	Lauric A.	1.5	50.0	2.25	4.0	93.7
12	ARP-70	Stearic A.	1.5	50.0	2.18	2.6	94.1
13	ARP-71	Isostearic	1.5	50.0	2.63	1.8	70.0
14	ARP-72	Oleic A.	1.5	50.0	2.70	1.9	74.9
15	ARP-76	Undecylenic A.[7]	1.5	50.0	2.38	4.7	96.8
16	ARP-77	Myristic A.	1.5	50.0	2.36	3.5	95.1
17	ARP-83	Palmitic A.	1.5	50.0		2.0	79.3

[1] - Commercial PCC a stable slurry of Aragonite (Opacarb® A40 ex SMI – USA).
[2] - CaCO3 (spacer) - a GCC (Calcite ex Polichrom Ltd. – Israel).
[3] – Calculated as the acid form, based on the CaCO3.
[4] – Measured according to Example 14 (E) in pure water, after calcining at 500°C for eight hours.
[5] – Measured at 60° with a Glossmeter (Minigloss 101N ex Sheen Instruments – England).
[6] – The hiding power of a 90μ layer was measured with a reflectometer (Ref. 310 Sheen-Opac ex Sheen Instruments – England).
[7] – This compound, for example, can be brominated and thus serves also as a flame retardant.

Notes:

1. The gloss increases as the v% of the CO_2 in the feed gas increases.
The gloss increases as the wt% of the active agent increases.
The gloss increases as the specific gravity (S.G.) of the PCC decreases.
These facts are particularly important in controlling the PCC of the present invention, and more specifically, in formulating high-gloss paper coatings on the one hand and it is particularly important in formulating low-gloss paints on the other hand.
2. The opacity increases as the wt% of the active agent increases.
The opacity increases as the V% of the air in the feed gas increases.
The opacity increases as the specific gravity (S.G.) of the PCC decreases.
n-Decanoic acid seems to exhibit, thus far, the best performance, however, the optimal w% seems to be in the range between 1.5 wt% to 3 wt% for this purpose of forming products of high hiding power.

EXAMPLE 16 – The preparation of the Plastic (Polypropylene Copolymer - PP) Formulations

The composition of the various formulations was as follows: 40% Filler, 0.3% antioxidant (Irganox B225 ex Ciba Specialty Chemicals - Switzerland), 0.5% lubricant (Wax PE 520 ex Hoechst-Celanese - USA) and 59.2% polypropylene copolymer (Capilene-TR50 ex Carmel Olefins - Israel).

(A) Preparation of the Particulate Precipitated Aragonite

Three samples of particulate precipitated aragonite of the present invention were used and three of the top quality commercial samples were used for comparison. The preparation parameters of the aragonite samples and their properties are given in Table 25, as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.)
2. pH = 9.5.
3. Temperature = 90°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5; 1; 2 wt.% based on $CaCO_3$.

Table 25 - the results of EXAMPLE 16(A)

#	Sample Code	Active agent	(wt.%)	Aragonite Aragonite+Calcite XRD	D_{90}[1] μ	B** (%)	SSA (BET) m^2/g
1	AR-213	Decanoic Acid	0.5*	93-96%	5.92	95.8	3.6
2	AR-214	Decanoic Acid	1.0*	93-96%	4.38	98.3	6.4
3	AR-215	Decanoic Acid	2.0*	96-98%	1.56	98.2	12.8

* - 50ppm of phosphoric acid were used in addition to the decanoic acid to increase the aspect ratio of the acicular aragonite.
** - Brightness.
[1] – The PCC of the present invention has not undergone any size reduction prior to its use, except the size reduction that may happen during regular operations.

(B) Compounding of the Plastic (Polypropylene Copolymer) Formulations

The formulations were processed in a co-rotating twin-screw compounder (L/D = 24 ex Dr. Collin – Germany). The compounding conditions are given in Table 26, as follows:

Table 26 - the compounding conditions of EXAMPLE 16(B)

#	Filler	Melt Temp. (°C)	Screws Speed (rpm)	Pressure (bar)	Torque (N.m)
1	AR-215	203	200	16±5	42±5
2	AR-214	203	200	15±5	40±2
3	AR-213	202	200	18±5	43±2
4	OM-95[A]	201	175	30±5	63±2
5	UPCC[B]	203	174	30±5	60±3
6	UTALC[C]	202	195	17±2	49±2

[A]– Commercial ultrafine stearic acid coated - UFT 95 GCC natural calcite (95 wt% pass 2μ size) ex Omya-Pluess-Staufer - Switzerland.
[B] – Commercial ultrafine stearic acid coated - Ultraflex PCC calcite ex SMI - USA.
[C] – Commercial ultrafine talc – Ultratalc 609 ex SMI - USA.

Note:
The results of the compounding step, in Table 16b, indicate that the PCC of the present invention is superior over the commercial products of the top qualities and top prices in the market.

(C) Injection of the Plastic (Polypropylene Copolymer) Formulations

The resulting granules were fed to an injection machine (25 t ex Dr. Boy – Germany). Specimens of 127x12.7x3.2 mm we produced. The injection conditions are given in Table 27 as follows:

Table 27 - the compounding conditions of EXAMPLE 16c

#	Filler	Temp. (°C)	Injection Speed (cm^3/sec.)	Injection Pressure (bar)	Injection Pressure (bar)
1	AR-215	170-180	66	250	250
2	AR-214	170-180	66	250	250
3	AR-213	170-180	66	250	300
4	OM-95[A]	170-180	66	250	300
5	UPCC[B]	170-180	66	400	400
6	UTALC[C]	170-180	66	400	400

[A] – a commercial ultrafine stearic acid coated GCC ex Omya-Pluess-Staufer - Switzerland.
[B] – a commercial ultrafine stearic acid coated - Ultraflex PCC ex SMI - USA.
[C] – a commercial ultrafine talc – Ultratalc 609 ex SMI - USA.

Note:
Only OM-95 behaves quite close to the PCC of the present invention (AR-213, Ar-214 and AR-215) in the injection compartment. The relatively (very) expensive talc is unable to compete with AR-213, Ar-214 and AR-215.

(D) The Mechanical Tests

The resulting specimens were conditioned at 25°C under 50% RH for at least 72 hrs. before testing them.

Two test were performed as follows:

Flexure testing (3 point) was conducted according to ASTM D-790.

Impact testing – Izod notched was conducted according to ASTM D-256.

The results are given in table 28, as follows:

Table 28 - the results of the mechanical tests of EXAMPLE 16d

#	Filler	Flex. Modulus (Mpa)	Impact (J/m)
0	-*	793	538
1	AR-215	1603±60	225±21.7
2	AR-214	1872±90	281±18.7
3	AR-213	1735±31	397±14.5
4	OM-95[A]	1107±20	192±20.4
5	UPCC[B]	1006±13	51±6.4
6	UTALC[C]	1749±54	151±5.3

*- Capilene – TR50 as reported by its producer.
A- a commercial ultrafine stearic acid coated GCC ex Omya-Pluess-Staufer - Switzerland.
B- a commercial ultrafine stearic acid coated - Ultraflex PCC ex SMI - USA.
C- a commercial ultrafine talc – Ultratalc 609 ex SMI - USA.

Notes:

1. Fillers are usually added to the polypropylene (PP) formulations to increase their flexural modulus. In the proper loading range, the higher the concentration of the filler, the higher is the flexural modulus. However, as the concentration of the filler increases, the Izod impact characteristics are decreased dramatically. Namely, the final loading of the filler in the polymer is the result of optimizing both characteristics of the final (consumer) products. Under the same experimental conditions, the particulate precipitated calcium carbonate of the present invention (AR-213, Ar-214 and AR-215) are by far superior over commercial products of the highest quality in the market.
2. The overall properties of the PCC of the present invention are superior over the commercial products of top qualities in the market, as it may leads to faster operations and to better (consumer) products.

EXAMPLE 17 – Adsorption Experiments Using the PCC of the present invention

The PCC/GCC particles of the prior art can adsorb limited quantities of liquids and in all cases that will take place quite fast onto their surface.

The PCC of the present invention exhibits a varied behavior, depending on the environment at which these particles are located.

(A) The PCC Particles of the Present Invention in the Gas Phase

The results that were obtained by using the gas pycnometer to determine the specific gravity (S.G.) of the product of the present invention (c. f. EXAMPLE 14 (D)) do not indicate at all that these particles contain some kind of "pores" or "bubbles" or "blisters" to any extend. However, the following results will demonstrate that this view is entirely wrong.

(B) The PCC Particles of the Present Invention in Stable Aqueous Dispersions

The process set points - continuous mode of operation:

1. Rotor Speed = 1200 rpm (Rotor Diameter = 10 cm)
2. pH = 9.5±0.2
3. Temperature = 85°C±2
4. Carbon dioxide flow rate = 2.5 m^3/hr.
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 80 - 100 L.P.H. (to maintain the preset pH value).
6. CO_2 (v%) in the feed gas=30%
7. Active agent concentration = decanoic acid; 1.5 wt.% based on $CaCO_3$.
8. Reactor Volume=50 l. (Diameter=30 cm).
9. The product (of the present invention) – ARP-73

Preparation of Stable Slurries (60-70 wt%) in Water:

The wet cake of ARP-73, which was obtained after dewatering of the product, was mixed with about 2 wt% dispersant (resulting in calculated ~1:1 dry weight ratio; Dispex N-40 (~45 wt% solids) ex Allied Colloids – GB) and water in a 10 l. (d=30 cm) tank that was equipped with laboratory dissolver (DVH-020-18/6; 2.5 HP ex a Dantco Inc. - USA; rotor diameter=10 cm) for 60 mins. At 1200 rpm. The resulting slurries exhibit the following characteristics:

Table 29 – the results of EXAMPLE 17 (B)

Sample Code	Solids In Slurry (wt%)[1]	S.G. of Slurry (g/cm^3)[4]		S.G. of Solids ARP-73 (g/cm^3)[1]
		After Preparation[1]	After 7 Days[2]	
ARP-73-1	60.2	1.47	1.47	2.13
ARP-73-2	69.3	1.61	1.61	2.20
ARP-73-3	63.0	1.55	1.68[3]	2.30

[1] - Was measured and/or calculated immediately after the preparation of the slurry.
[2] - Was measured and calculated.
[3] - The addition of 2 wt% sodium dioctylsulfosuccinate (75% in ethanol; ex Cytec – USA) - a potent wetting agent - to the water at the end of the preparation stage (+ a short stirring thereafter), led to the formation of a very dense and viscose mass after 7 days (most of the water have been absorbed by the PCC of the present invention), which could not be stirred. This mass was disintegrated by adding more of the wetting agent and stirring the mass. The S.G. was then measured and calculated to be >2.79 g/cm^3. Such behavior is unprecedented in the prior art of PCC/GCC products.
[4] - The low S.G. values are also observed in the paint compositions containing the products of the present invention, which gives rise to an additional advantage, as was explained already in EXAMPLE 15.

(C) Dispersions of the PCC Particles of the Present Invention in Organic Solvents

Attempts to obtain stable slurries of the PCC of the present invention in organic solvents such as alcohols (e.g. ethanol, isopropanol), ketones (e.g. acetone, methyl ethyl ketone), esters (e.g. methyl acetate, ethyl acetate), aromatic solvents (e.g. toluene, xylene, chlorobenzene, o-dichlorobenzene), and many others, result in the formation of mixtures in which the specific gravity (S.G.) of the PCC particles is >2.5 g/cm^3 (usually, water and oils (e.g. those that are mentioned as liquids in Example 14), permeate very slowly during very long periods and in some cases it is impractical to measure their permeation rates). More polar solvents such as ethylene glycol penetrate more slowly into the PCC of the present invention, and eventually the S.G. values reach the ultimate value that characterizes calcite, and especially aragonite, calcium carbonate (namely, ~2.7 – 2.9 g/cm^3, depending on the specific crystallographic purity of the tested products). Naturally, the increase of the S.G. is dependent on many factors

such as pressure, temperature, viscosity, surface tension, purity, and naturally the quality of the PCC product of the present invention.

It is worthwhile noting that the unique properties of the original PCC particles of the present invention are fully restored once the organic solvent is evaporated to dryness, and this product can be used in the same application or another one as the original sample. More specifically, after the removal of e.g. acetone, toluene, or ethyl acetate, all the properties of a used sample e. g. of AR-120, matched the original sample.

The phenomenon described in this EXAMPLE 17 leads to the conclusion that the PCC of the present invention can readily be used as an adsorbent for liquids (solvent), as a carrier (encapsulant) for liquids and solids (by dissolving them in a suitable solvent; allowing the solution to penetrate into the "pores" of the PCC; and removing the solvent by e.g. evaporation or dissolution of the solvent in another solvent that reduces the solubility of the substrate. The PCC of the present invention can encapsulate many compounds, including e.g. pharmaceuticals (medicines), agrochemicals, flavors, fragrances and sunscreen agents (this PCC itself is particularly suitable for protecting the human skin, once its particles are fine-tuned for that purpose. Due to the embedded "pores" in the PCC of the present invention, this task of fine-tuning the PSD to meet the requirements to protect from incoming light at 300-400 mμ, is expected to be much less expensive than of e. g. the TiO_2, which is used for this purpose quite often). Therefore, the PCC of the present invention offers two functions in one material, namely, encapsulation and efficient light dispersion). Moreover, the "porous" nature of this PCC makes it a preferable candidate to serve as a filler, a builder and/or an anticaking agent in e. g. powder detergents, etc.

To summarize, the PCC of the present invention can serve in any capacity that calcium carbonate particles of the prior art serve, and additionally it possesses many advantages due to its "porous" nature.

(C) <u>The "porous" Nature of calcined PCC Particles of the Present Invention - at 500°C for Eight Hours.</u>

By merely coating the surfaces of GCC/PCC particles of the prior art with e.g. n-decanoic acid, their S.G. is reduced due to adhering bubbles (c.f. EXAMPLE

14 (H), Tests #82 and #83). However, the performance such prior art products iss inferior to the products of the present invention. In particular, their fundamental characteristics are revealed once they are calcined at 500°C for eight hours to remove all organic compounds, when the calcinations product has an S.G. >2.5 g/cm^3,(c.f. EXAMPLE 14(E), Tests #30 and #32), whereas the products of the present invention always remain "light" and "porous" (S.G. <2.5 g/cm^3). To further demonstrate this, we compared various calcined prior art products with products of the present invention. The kinetics of increasing the specific gravity of the calcined samples in ethylene glycol and in water were conducted as follows: the selected samples were calcined at 500°C for eight hours and were introduced into excess of liquid (c. f. EXAMPLE 14 (E)). The S.G. results were recorded at 5 mins, 24 hrs. and 48 hrs, after mixing with the respective liquids. The results are given in Table 30, as follows:

Table 30 – the results of EXAMPLE 17 (C)

Sample Code	S.G. in Ethylene glycol g/cm^3		
	5 mins.	24 hrs.	48hrs
GCC-8[1]	>2.7	>2.7	>2.7
GCC-8[2]	>2.7	>2.7	>2.7
PCC[3]	>2.7	>2.7	>2.7
PCC[4]	>2.7	>2.7	>2.7
ARP-35[5]	2.25	2.35	2.38
ARP-36[5]	2.13	2.22	2.27
ARP-62-1[5]	2.17	2.24	2.30
Sample Code	S.G. in Water g/cm^3		
	5 mins.	24 hrs.	48hrs
GCC-8[1]	>2.7	>2.7	>2.7
GCC-8[2]	>2.7	>2.7	>2.7
PCC[3]	>2.7	>2.7	>2.7
PCC[4]	>2.7	>2.7	>2.7
ARP-35[5,6]	2.25	2.49	2.54
ARP-36[5,6]	2.36	2.40	2.46
ARP-62-1[5]	2.01	2.29	2.31

[1] -"Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom – Israel.
[2] – "Girulite-8" CaCO3 powder (d50=3.5 microns) ex Polychrom - Israel, which was coated using 2 wt% n-decanoic acid.
[3] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.
[4] – Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40, which was coated using 2 wt% n-decanoic acid.
[5] – Their production is described already (c. f. EXAMPLE 14 (E)).
[6] - 2 wt% sodium dioctylsulfosuccinate were added to the water.

Notes:

1. Determination of the S.G. of the calcined PCC of the present invention in water seems to be a simple, fast, and quite accurate method to distinguish between the products of the of the present invention, and therefore, the process of the present

invention, and the product of the prior art, and therefore, the process of the prior art (also, c. f. EXAMPLE 14 (F)).

2. The "porous' product of the present invention may absorb considerable quantities of solvents (>50% of its weight).

3. The existence of "pores" in the PCC of the present invention has been established by direct and indirect evidence. However, it is not of much consequence if we are still not too accurate in depicting the exact properties that are responsible for the effects that were encountered.

While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.

CLAIMS

1. A process for producing a particulate precipitated aragonite calcium carbonate, which comprises reacting an aqueous calcium hydroxide slurry with a gas selected from the group consisting of carbon dioxide and a gas containing it, wherein the parameters of said process, including at least one preselected active agent, mode of operation, operating concentrations of raw materials, operating temperature, operating mixer speed and operating pH, are such that (A) the specific gravity of the product after drying for 12 hours at $120^{o}C$ is <2.5 g/cm^3; and (B) the specific gravity of this dry product after ignition for eight hours at $500^{o}C$ is <2.5 g/cm^3.

2. A process according to claim 1, in which said at least one active agent is selected from the group consisting of carboxylic acids of formula RCOOH, where R is an organic group containing 7-20 carbon atoms, their carboxylate salts, their acid anhydrides, their esters, their acyl halides and their ketenes.

3. A process according to claim 2, in which said at least one active agent is selected from the group consisting of carboxylic acids of formula $C_nH_{2n+1}COOH$, where n is 8-17, their carboxylate salts, their acid anhydrides, their esters, their acyl halides and their ketenes of the formula $C_nH_{2n+1}C{=}C{=}O$, where n is 7-16.

4. A process according to claim 2, which is further characterized by the following features:

(a) said at least one active agent is selected from the group consisting of carboxylic acids of formula $CH_3(CH_2)_nCOOH$, where n is 7-16, their carboxylate salts, their acid anhydrides, their esters, their acyl halides and their ketenes of the formula $CH_3(CH_2)_nC{=}C{=}O$, where n is 6-15;

(b) said concentration of the at least one active agent is within the range between 0.2 wt.% and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate;

(c) said slurry contains calcium hydroxide in a concentration within the range of from 3 to 30 wt.%;

(d) said pH is within the range of from 8 to 11;

(e) said temperature is in the range between 60°C and the boiling temperature of the reaction mixture;

(f) said mode of operation is selected from a continuous and a semi-continuous (intermittent) mode of operation;

(g) said mixer peripheral speed (tip-speed) is above 5 m/sec.;

(h) said at least one active agent is added in a manner selected from introduction into the carbonation reactor and premixing with said calcium hydroxide slurry prior to reaction with said gas.

5. A process according to claim 4, which is further characterized by at least one of the following features:

(a) said at least one active agent is selected from the group consisting of carboxylic acids of formula $CH_3(CH_2)_nCOOH$, where n is 7-16, and the calcium salts thereof;

(b) said concentration of the at least one active agent is within the range between 0.3 wt.% and 5 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate;

(c) said slurry contains calcium hydroxide in a concentration within the range of from 4 to 20 wt.%;

(d) said pH is within the range of from 9 to 10;

(e) said temperature is in the range between 80°C and the boiling temperature of the reaction mixture;

(f) said mode of operation is a continuous mode of operation.

6. A process according to claim 5, which is further characterized by at least one of the following features, namely:

(a) said active agent is selected from the group consisting of decanoic acid and the calcium salts thereof,

(b) said concentration of said at least one active agent is within the range between 0.4 wt.% and 3 wt.%, calculated as carboxylic acid and based on the weight of calcium carbonate,

(c) said temperature is in the range between 90°C and the boiling temperature of the reaction mixture, and

(d) said slurry contains calcium hydroxide in a concentration within the range of from 5 to 15 wt.%.

7. A process according to claim 2, which is further characterized by at least feature (a) of the following features:

(a) said at least one active agent is selected from the group consisting of carboxylic acids of formula $C_nH_{2n-1}COOH$, where n is 8-17, their carboxylate salts, their acid anhydrides, their esters, their acyl halides and their ketenes of the formula $C_nH_{2n-1}C=C=O$, where n is 7-16;

(b) said concentration of the at least one active agent is within the range between 0.2 wt.% and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate;

(c) said slurry contains calcium hydroxide in a concentration within the range of from 3 to 30 wt.%;

(d) said pH is within the range of from 8 to 11;

(e) said temperature is in the range between 60°C and the boiling temperature of the reaction mixture;

(f) said mode of operation is selected from a continuous and a semi-continuous (intermittent) mode of operation;

(g) said mixer peripheral speed (tip-speed) is above 5 m/sec.;

(h) said at least one active agent is added in a manner selected from introduction into the carbonation reactor and premixing with said calcium hydroxide slurry prior to reaction with said gas.

8. A process according to claim 7, which is further characterized by at least one of the following features, namely:

(a) said active agent is selected from the group consisting of undecylenic acid and the calcium salts thereof,

(b) said concentration of said at least one active agent is within the range between 0.4 wt.% and 3 wt.%, calculated as carboxylic acid and based on the weight of calcium carbonate,

(c) said temperature is in the range between 90°C and the boiling temperature of the reaction mixture, and

(d) said slurry contains calcium hydroxide in a concentration within the range of from 5 to 15 wt.%.

9. A process according to claim 1, which is conducted as a flotation process in a flotation cell.

10. A process according to claim 9, and substantially as hereinbefore described with reference to Figure 3 of the attached drawings.

11. A particulate precipitated aragonite produced by the process of claim 1.

12. A particulate precipitated aragonite according to claim 11, which is characterized by at least one of the following features:

(i) it contains at least one calcium salt of carboxylic acids selected from those of the general formulae $C_nH_{2n+1}COOH$ and $C_nH_{2n-1}COOH$, where n is 8-17, in an amount between 0.2 and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate;

(ii) it has an XRD spectrum substantially in accordance with Figure 5 of the attached drawings.

13. A particulate precipitated aragonite according to claim 12, which contains at least one calcium salt of carboxylic acids selected from those of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7-16, in an amount between 0.2 and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate.

14. A particulate precipitated aragonite according to claim 11, having a specific gravity <2.3 g/cm^3 after drying at 120^{o}C for twelve hours, and a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500^{o}C.

15. A particulate precipitated aragonite according to claim 14, having a specific gravity <2.0 g/cm^3 after drying at 120^{o}C for twelve hours.

16. A particulate precipitated aragonite according to claim 15, having a specific gravity <1.8 g/cm^3 after drying at 120^{o}C for twelve hours.

17. A particulate precipitated aragonite according to claim 16, having a specific gravity <1.5 g/cm^3 after drying at 120^{o}C for twelve hours.

18. A particulate precipitated aragonite according to claim 11, having a specific gravity <2.1 g/cm^3 after drying at 120^{o}C for twelve hours, and a specific gravity <2.1 g/cm^3 after ignition for eight hours at 500^{o}C.

19. A particulate precipitated aragonite which has (A) a specific gravity <2.5 g/cm^3 after drying for 12 hours at 120^{o}C, and (B) a specific gravity <2.5 g/cm^3 after ignition for eight hours at 500^{o}C of the product dried in (A).

20. A particulate precipitated aragonite which has (A) a specific gravity <2.3 g/cm^3 after drying at 120 ^{o}C, and (B) a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500^{o}C of the product dried in (A).

21. A particulate precipitated aragonite which has a specific gravity <2.1 g/cm^3 after drying at 120^{o}C for twelve hours, and a specific gravity <2.1 g/cm^3 after ignition for eight hours at 500^{o}C.

22. A particulate precipitated aragonite which has (A) a specific gravity <1.8 g/cm^3 after drying at 120 ^{o}C, and (B) a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500^{o}C of the product dried in (A).

23. A particulate precipitated aragonite which has (A) a specific gravity <1.5 g/cm^3 after drying at 120 °C, and (B) a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500°C of the product dried in (A).

24. A particulate precipitated aragonite which has (A) a specific gravity <1.5 g/cm^3 after drying at 120 °C, and (B) a specific gravity <2.1 g/cm^3 after ignition for eight hours at 500°C of the product dried in (A).

25. A particulate precipitated aragonite which has a specific gravity <2.5 g/cm^3 after ignition for eight hours at 500°C.

26. A particulate precipitated aragonite which has a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500°C.

27. A particulate precipitated aragonite which has a specific gravity <2.1 g/cm^3 after ignition for eight hours at 500°C.

28. A particulate precipitated aragonite according to any one of claims 19 to 27, which is characterized by at least one of the following features:
(I) it contains at least one calcium salt of carboxylic acids selected from those of the general formulae $C_nH_{2n+1}COOH$ and $C_nH_{2n-1}COOH$, where n is 8-17, in an amount between 0.2 and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate;
(ii) it has an XRD spectrum substantially in accordance with Figure 5 of the attached drawings.

29. A particulate precipitated aragonite according to claim 28, which contains at least one calcium salt of carboxylic acids selected from those of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7-16, in an amount between 0.2 and 10 wt.%, calculated as carboxylic acid(s) and based on the weight of calcium carbonate.

30. A particulate precipitated aragonite according claim 28, which contains at least one calcium salt of carboxylic acids selected from those of the general

formula: $C_nH_{2n-1}COOH$, where n is 8-17, in an amount between 0.2 and 10 wt.%, calculated as $C_nH_{2n-1}COOH$ and based on the weight of calcium carbonate.

31. A particulate precipitated aragonite according to any one of claims 11 to 27, of crystallographic purity (aragonite/(aragonite + calcite)) at least 90%.

32. A particulate precipitated aragonite according to any one of claims 11 to 27, of crystallographic purity (aragonite/(aragonite + calcite)) <90%.

33. A process according to any one of claims 1 to 10, wherein said specific gravity is determined substantially as described in Example 14 (F).

34. A particulate precipitated aragonite according to any one of claims 11 to 27, wherein said specific gravity is determined substantially as described in Example 14 (F).

35. A coating composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

36. A coating composition according to claim 35, which comprises substantially dry particulate precipitated aragonite.

37. A coating composition according to claim 35, which comprises particulate precipitated aragonite in aqueous dispersion.

38. A paper composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

39. A paper composition according to claim 38, which comprises substantially dry particulate precipitated aragonite.

40. A paper composition according to claim 38, which comprises particulate precipitated aragonite in aqueous dispersion.

41. A plastics composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

42. A plastics composition according to claim 41, which comprises substantially dry particulate precipitated aragonite.

43. A rubber composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

44. A rubber composition according to claim 43, which comprises substantially dry particulate precipitated aragonite.

45. An adsorbent composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

46. An adsorbent composition according to claim 45, which comprises substantially dry particulate precipitated aragonite.

47. A powder detergent composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

48. A powder detergent composition according to claim 47, which comprises substantially dry particulate precipitated aragonite.

49. A pharmaceutical composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

50. A pharmaceutical composition according to claim 49, which comprises substantially dry particulate precipitated aragonite.

51. A pharmaceutical composition according to claim 49, which comprises particulate precipitated aragonite in aqueous dispersion.

52. An agrochemical composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

53. An agrochemical composition according to claim 52, which comprises substantially dry particulate precipitated aragonite.

54. An agrochemical composition according to claim 52, which comprises particulate precipitated aragonite in aqueous dispersion.

55. A flavor composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

56. A flavor composition according to claim 55, which comprises substantially dry particulate precipitated aragonite.

57. A flavor composition according to claim 55, which comprises particulate precipitated aragonite in aqueous dispersion.

58. A fragrance composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

59. A fragrance composition according to claim 58, which comprises substantially dry particulate precipitated aragonite.

60. A fragrance composition according to claim 58, which comprises particulate precipitated aragonite in aqueous dispersion.

61. A food composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

62. A food composition according to claim 61, which comprises substantially dry particulate precipitated aragonite.

63. A food composition according to claim 61, which comprises particulate precipitated aragonite in aqueous dispersion.

64. A feed composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

65. A feed composition according to claim 64, which comprises substantially dry particulate precipitated aragonite.

66. A feed composition according to claim 64, which comprises particulate precipitated aragonite in aqueous dispersion.

67. A sunscreen composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

68. A sunscreen composition according to claim 67, which comprises substantially dry particulate precipitated aragonite.

69. A sunscreen composition according to claim 67, which comprises particulate precipitated aragonite in aqueous dispersion.

70. A conductive powder composition which comprises a particulate precipitated aragonite as defined in any one of claims 11 to 27.

71. A conductive powder composition according to claim 70, which comprises substantially dry particulate precipitated aragonite.

72. A particulate precipitated aragonite, which after drying it for 12 hours at 120°C, has a Loose Bulk Density (L.B.D.) <0.4 g/cm^3.

73. A particulate precipitated aragonite according to claim 72, wherein said L.B.D. is determined substantially as described in Example 14 (G).

ABSTRACT

Disclosed is a novel form of particulate precipitated aragonite, a novel process for producing it and compositions containing it.

268 297 #4

2111-___ Nixon & Vanderhye P.C. (1000)
(Docket= Non-Assigned/Foreign) Page 1

RULE 63 (37 C.F.R. 1.63)
INVENTORS DECLARATION FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT

the specification of which (check applicable box(s)):

☒ is attached hereto

☐ was filed on _____ as U.S. Application Serial No. _____ (My Dkt. No. 2111-___)

☐ was filed as PCT international application No. _____ on _____

And (if applicable to U.S. or PCT application) was amended on _____

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed or, if no priority is claimed, before the filing date of this application:

Priority Foreign Application(s):

Application Number	Country	Day/Month/Year Filed

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

Application Number	Date/Month/Year Filed

I hereby claim the benefit under 35 U.S.C. 120/365 of all prior United States and PCT international applications listed above or below and, insofar as the subject matter of each of the claims of this application is not disclosed in such prior applications in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose material information as defined in 37 C.F.R. 1.56 which occurred between the filing date of the prior applications and the national or PCT international filing date of this application:

Prior U.S./PCT Application(s):

Application Serial No.	Day/Month/Year Filed	Status: patented, pending, abandoned
☐ 08/513,749	March 6, 2000	Pending

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon. And on behalf of the owner(s) hereof, I hereby appoint NIXON & VANDERHYE P.C., 1100 North Glebe Rd., 8th Floor, Arlington, VA 22201-4714, telephone number (703) 816-4000 (to whom all communications are to be directed), and the following attorneys thereof (of the same address individually and collectively customer/present attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent: Arthur R. Crawford, 25327; Larry S. Nixon, 25640; Robert A. Vanderhye, 27076; James T. Hosmer, 30184; Robert W. Faris, 31352; Richard C. Bowes, 32770; Mark E. Nusbaum, 33141; Manuel J. Keenan, 33108; Bryan H. Davidson, 33281; Stanley C. Spooner, 27393; Laurence C. Maitland, 34005; Duane M. Byers, 33363; Judy H. Nelson, 33481; John R. Lastova, 33149; H. Warren Burnam, Jr. 29366; Thomas E. Byrne, 32205; Mary J. Wilson, 32955; J. Scott Davidson, 33405; Alan M. Kagen, 36178; Robert A. Molan, 29834; B. J. Sadoff, 36663; James D. Berquist, 34776; Updeep S. Gill, 37334; Michael J. Shea, 34725; Donald L. Jackson, 41090; Michelle N. Lester, 32331; Frank P. Presta, 19828; Joseph S. Presta, 35329; Jessica A. Rose, 37715. I also authorize Nixon & Vanderhye to delete any attorney name/numbers no longer with the firm and to act and rely solely on instructions directly communicated from the person, assignee, attorney, firm, or other organization owning instructions to Nixon & Vanderhye on behalf of the owner(s).

1. Inventor's Signature: _____ Date: February 6, 2001
Inventor: Jesus (first) M (mi) Yoshi (last) Israel (citizenship)
Residence: (city) Haifa 34722 (state/country) Israel
Post Office Address: 75 Yaakobson Street, Haifa 34722 Israel
(Zip Code) N/A

2. Inventor's Signature: _____ Date: _____
Inventor: N/A (first) (mi) (last) (citizenship)
Residence: (city) _____ (state/country) _____
Post Office Address: _____
(Zip Code) _____

FOR ADDITIONAL INVENTORS, check box ☐ and attach sheet with same information and signature and date for each.

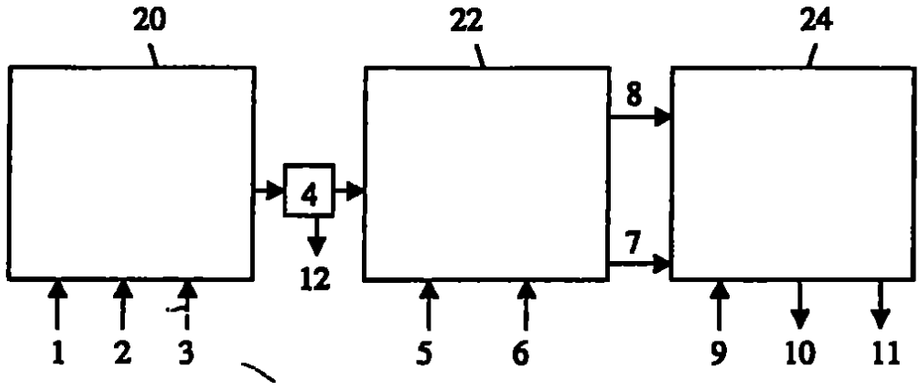

FIGURE 1

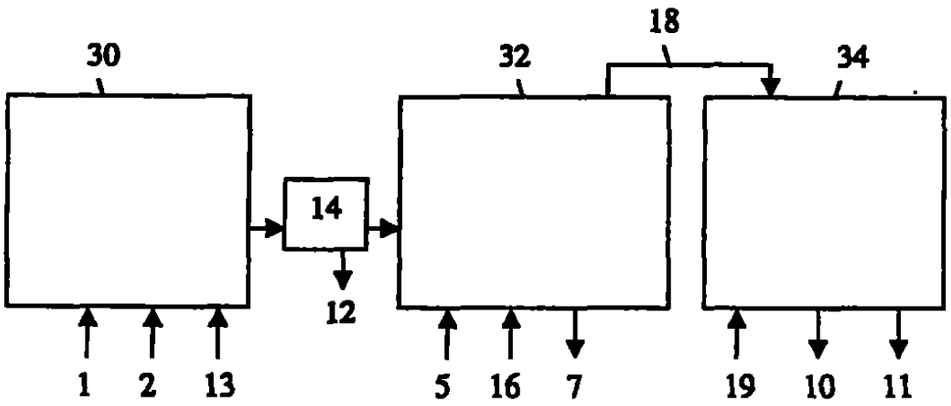

FIGURE 2

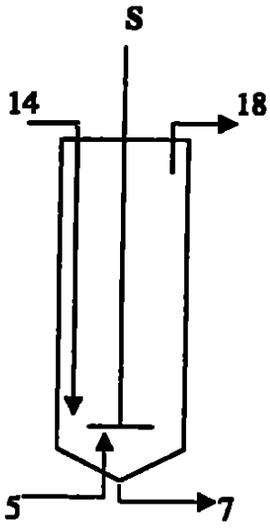

FIGURE 3

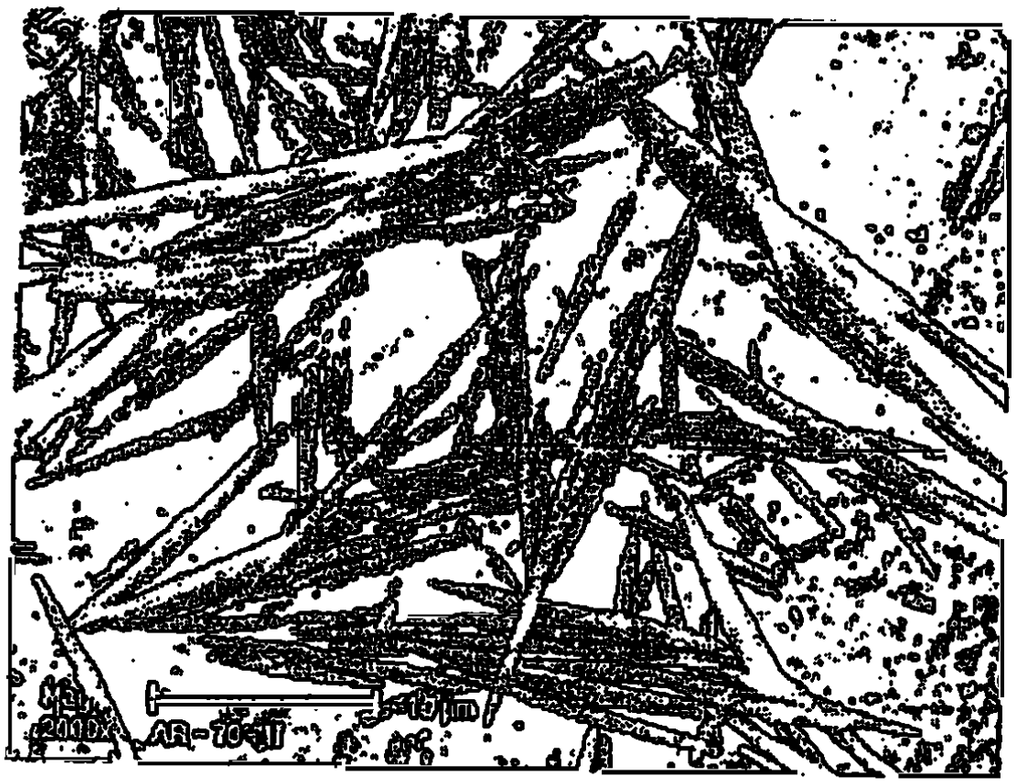

FIGURE 4

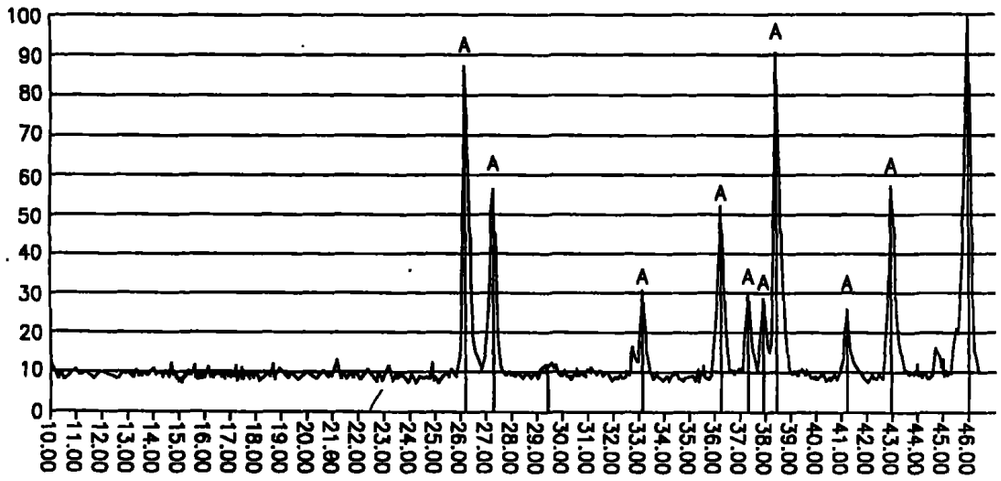
100
90
80
70
60
50
40
30
20
10
0
A
A
A
A
A
A
A
A
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
20.00
21.80
22.00
23.00
24.00
25.00
26.00
27.00
28.00
29.00
30.00
31.00
32.00
33.00
34.00
35.00
36.00
37.00
38.00
39.00
40.00
41.00
42.00
43.00
44.00
45.00
46.00

FIGURE 5

SEM Picture of ARP-76, which contains ~97% Aragonite

FIGURE 6

XRD spectrum of ARP-76, which contains ~97% Aragonite

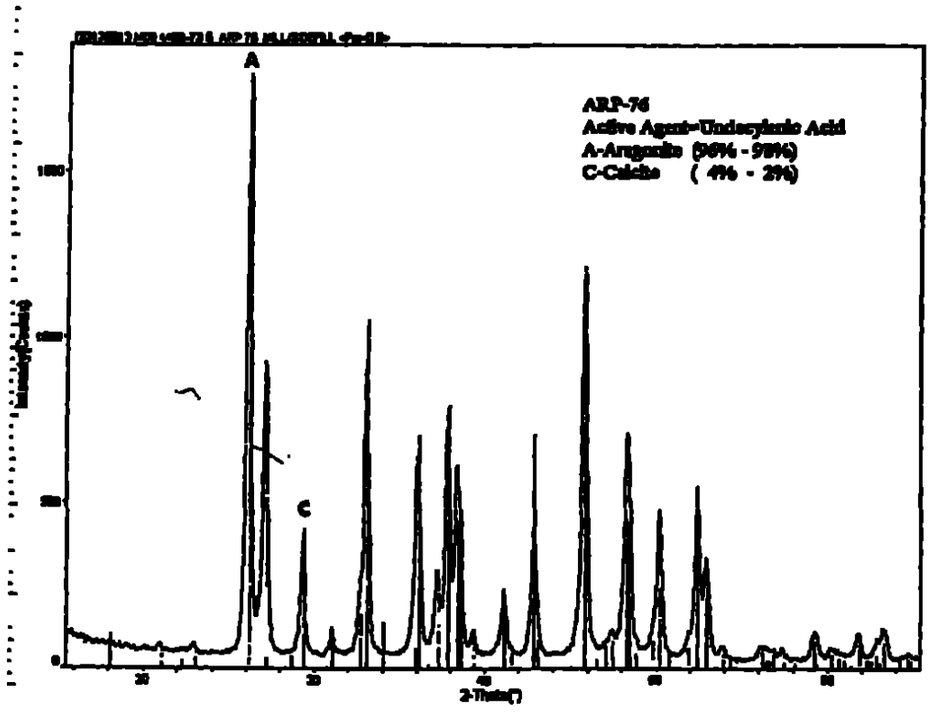

FIGURE 7

SEM Picture of ARP-70 (50% aragonite + 50% Calcite)

FIGURE 8

XRD spectrum of ARP-70, which contains ~50% Aragonite

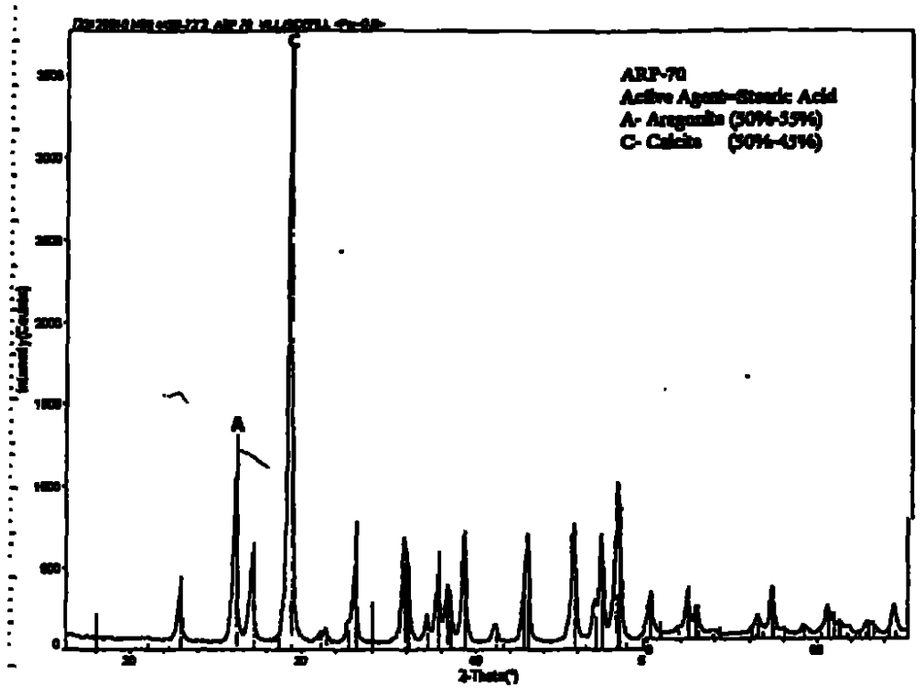

FIGURE 9

278

PTO 163517

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

February 09, 2001

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: *09/519,749*
FILING DATE: *March 06, 2000*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

L. Edelen

L. EDELEN
Certifying Officer

jc490 U.S. PTO
03/06/00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING APPLICATION UNDER 37 CFR 53(b)
WITHOUT FILING FEE OR EXECUTED INVENTOR'S DECLARATION

Assistant Commissioner for Patents
Washington, D.C. 20231

Atty. Dkt. 2111-13
Date: March 6, 2000

jc464 U.S. PTO
09/519749
03/06/00

Sir:

This is a request for filing a new PATENT APPLICATION under Rule 53(b) entitled:
PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT
without a filing fee and/or without an executed inventor's oath/declaration.
This application is made by the below identified inventor(s). Attached hereto are the following papers:

☒ An abstract together with
58 pages of specification and claims including
19 numbered claims and also attached is/are
5 sheets of accompanying drawings.
☐ This application is based on the following prior foreign application(s):

Application No.	Country	Filing Date

respectively, the entire content of which is hereby incorporated by reference in this application, and priority is hereby claimed therefrom.

☐ This application is based on the following prior provisional application(s):

Application No.	Filing Date

respectively, the entire content of which is hereby incorporated by reference in this application, and priority is hereby claimed therefrom.

☐ Certified copy/ies of foreign applications attached.
☐ This application is a ☐ continuation/☐ division/☐ continuation-in-part of application Serial No. , filed .
☐ Please amend the specification by inserting before the first line: --This application is a ☐ continuation/☐ division/☐ continuation-in-part of application Serial No. , filed , the entire content of which is hereby incorporated by reference in this application.--
☐ Please amend the specification by inserting before the first line: --This is a continuation of PCT application No. , filed , the entire content of which is hereby incorporated by reference in this application.--
☐ Please amend the specification by inserting before the first line: --This application claims the benefit of U.S. Provisional Application No. , filed , the entire content of which is hereby incorporated by reference in this application.--
☒ Preliminary amendment to claims (attached hereto), to be entered before calculation of the fee.
☐ Also attached.

1. Inventor: Isaac (first) MI YANIV (last) Israeli (citizenship)
Residence: (city) Haifa (state/country) Israel
Post Office Address: 75 Yekinton Street, Haifa, Israel
(incl zip code) 34792

2. Inventor: (first) MI (last) (citizenship)
Residence: (city) (state/country)
Post Office Address: , ,
(incl zip code)

NOTE: FOR ADDITIONAL INVENTORS, check box ☐ and attach sheet with same information.
Address all future communications to NIXON & VANDERHYE P.C., 1100 North Glebe Road, 8th Floor, Arlington, Virginia 22201.

1100 N. Glebe Road, 8th Floor
Arlington, Virginia 22201
Telephone: (703) 816-4000
Facsimile: (703) 816-4100

NIXON & VANDERHYE P.C.
By Atty.: Larry S. Nixon, Reg. No. 25,640

Signature: Larry S. Nixon

LSN:vc

8qy201l.DOC

305
15
280

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Isaac YANIV Atty. Ref.: 2111-13

Serial No. (To Be Assigned) Group:

Filed: March 6, 2000 Examiner:

For: **PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT**

* * * * * * * * * * * *

March 6, 2000

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

PRELIMINARY AMENDMENT

In order to place the above-identified application in better condition for examination, please amend the application as follows:

IN THE CLAIMS

Claim 11, line 1, delete "any of claims 7 to 10," and insert --claim 7--.

Claim 12, line 1, delete "any of claims 7 to 10," and insert --claim 7--.

Claim 15, line 1, delete "or claim 14".

Claim 16, line 1, delete "or claim 14".

Claim 17, line 1, delete "or claim 14".

Claim 18, line 1, delete "or claim 14".

Claim 19, line 1, delete "or claim 14".

REMARKS

Respectfully submitted,

NIXON & VANDERHYE P.C.

By: Larry S. Nixon

Larry S. Nixon
Reg. No. 25,640

LSN:vc
1100 North Glebe Road, 8th Floor
Arlington, VA 22201-4714
Telephone: (703) 816-4000
Facsimile: (703) 816-4100

282 B1 B01

Our Ref.: 2111-13
3PT283/10.3

U.S. PATENT APPLICATION

Inventor(s): Isaac YANIV

09519749 .030600

Invention: PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT

NIXON & VANDERHYE P.C.
ATTORNEYS AT LAW
1100 NORTH GLEBE ROAD
8TH FLOOR
ARLINGTON, VIRGINIA 22201-4714
(703) 816-4000
Facsimile (703) 816-4100

SPECIFICATION

PRECIPITATED ARAGONITE AND A PROCESS FOR PRODUCING IT

FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to a novel form of precipitated aragonite and to a novel process for producing it.

Various routes are known for the production of calcium carbonate, which finds use as a thickening material, as a filler, as an extender, and most of all as a pigment, in a variety of industries such as pharmaceuticals, plastics, adhesives, printing, coating (paint), paper, rubber and in filtration. For such purposes, there may be used ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC). PCC in general possesses advantages over GCC, in that it is economical to produce and its precise composition, or purity, can be more strictly controlled.

The most frequently used chemical process for producing PCC is based on the carbonation of aqueous suspensions of calcium hydroxide (also known as "milk of lime" or "slaked lime") with carbon dioxide gas, or with a carbon dioxide containing gas. This process gives rise to relatively pure precipitated calcium carbonate and is a preferred process, because there are no serious problems of contamination of the product with undesired salts, and moreover it can be controlled in order to adjust the properties of the final product. Thus, the process is based essentially on four stages: firstly, calcination of raw limestone to produce calcium oxide or "quicklime" and carbon dioxide gas or a carbon dioxide containing gas; secondly, "slaking" of the quicklime with water to produce an aqueous suspension of calcium hydroxide; thirdly, carbonation of the calcium hydroxide with carbon dioxide gas or a carbon dioxide containing gas; and finally, downstream operations such as dewatering, drying, deagglomeration, grinding, surface treatment, surface coating, mixing with other minerals (e.g. titanium dioxide, talc, kaolin, GCC, PCC – including aragonite PCC) and dyeing, which allow optimization of the properties of the precipitated calcium carbonate particles in order to be adapted to their intended uses.

Calcium carbonate can be precipitated from aqueous calcium hydroxide slurries or solutions in three different crystallographic forms (polymorphs): the vaterite form which is thermodynamically unstable, the aragonite form which is

metastable under normal ambient conditions of temperature and pressure, and the calcite form which is the most stable and the most abundant in nature. These forms of calcium carbonate can be prepared by carbonation of slaked lime by suitable variations of the process conditions.

The calcite form is easy to produce on industrial scales, as precipitated calcium carbonate particles. It exists in several different shapes, of which the most common are the rhombohedral shape and the scalenohedral shape.

Aragonite forms crystals having a length/width ratio (hereinafter - "aspect ratio") in the range between >1:1 and 100:1 of which a typical aspect ratio is 10, in which case the aragonite forms long, thin needles. Therefore, aragonite having a high aspect ratio may be denoted hereinafter - "acicular aragonite" or "needle-shaped aragonite". The production of aragonite is a slow process and is very difficult to control on an industrial scale.

PCC particles are used as thickening materials, fillers, extenders and, most of all, as inexpensive pigments. The latter use implies that a particularly desirable property of this material is its light scattering characteristics, in order to be able impart opacity and brightness to the products containing it. Such characteristics are optimized, when the pigment particles are very effectively dispersed and are apart by an average distance in the range between 0.2μm and 0.4μm in their final products, and their size distribution is in the range between 0.2μm and 0.4μm, namely, in the range of half a wavelength of the visible light. That means that either the production of the PCC should be adjusted to produce small particles in order to avoid expensive downstream particle size reduction operations and to cope with the expensive problems of dewatering and drying the product, or, alternatively, the process should be adjusted to produce large particles, and subsequently effect the downstream dewatering and grinding operations. In both cases, the production costs of precipitated calcium carbonate of pigment grades may be doubled or tripled just because of these unavoidable downstream steps.

High light scattering pigments currently available to the above-mentioned industries include titanium dioxide particles, which are very effective to scatter the light due to their relatively high refractive index (2.76; for the rutile form) and their

meticulously controlled particle size distribution of which median is in the range between 0.2μm and 0.4μm. However, this product is of a high specific gravity (~4.0g/cm^3), of a high surface area due to its small particles, and most of all, is quite expensive. Fine kaolin particles are also being used as pigments, but this product has a much lower refractive index (1.56), is of limited whiteness and is still relatively expensive. Particulate calcium carbonate is the ideal least expensive pigment and could replace much more of the titanium dioxide and kaolin pigments in their respective present applications, if it could be prepared in a form having improved light scattering properties.

Calcium carbonate pigments are produced in part by grinding coarse natural rocks and in part by precipitation processes. Of the precipitated calcium carbonate particles, a particulate precipitated aragonite is considered to be the most effective light scattering calcium carbonate pigment, of which refractive indices are 1.530, 1.681 and 1.685, depending on its crystallographic surfaces, its specific gravity is above 2.5g/cm^3, and is the most suitable for same applications. However, its production rate is characteristically very slow and its production conditions are very difficult to control, industrially.

While the majority of references, cited hereinafter, relate to the technology for producing a particulate precipitated aragonite, some of the references are included in order to better present the state of the art for the production of PCC more generally, including the downstream operations, which may be common to all these processes and also to the present invention.

1. U.S. Patent No. 2,081,112 (N. Statham et al.) describes a process for producing precipitated calcium carbonate by carbonating milk of lime with carbon dioxide containing gas, where the temperature in the gas absorber is maintained at 50-60°C, preferably around 55°C. It is recognized that the more violent the agitation in the gas absorber, the finer will be the product; the aim being to create a fine mist of calcium hydroxide slurry.

2 U.S. Patent No. 2,964,382 (G. E. Hall, Jr.) describes production of precipitated calcium carbonate by various chemical routes, in which calcium ions are contacted with carbonate ions in a precipitation zone, the process including

also carbonation of milk of lime with carbon dioxide gas. A high shear stator/rotor agitator is used to provide turbulence by rotating at a peripheral speed of at least 1160 feet per minute (589 cm per second) in the precipitation zone. Also, this patent teaches that it is desirable to operate the process at pH values of at least 8.5 and that at temperatures above 60°C, needle-shaped precipitated aragonite particles are formed, which however produce an adverse flow property effect.

3. U.S. Patent No. 3,320,026 (W. F. Waldeck) describes the production of various forms of precipitated calcium carbonate.

4. GB Patent No. 941,900 (assigned to Kaiser Aluminium & Chemical corporation) describes the production of precipitated aragonite particles, for use as a filter aid, by reacting continuously sodium carbonate solution and aqueous calcium hydroxide slurry at temperatures higher than 60°C in a multistage system. The product and the solution are withdrawn at the third stage from the bottom of the reactor, the product is then separated from the solution and part of the crystals are recycled to the various stages of the process as seeds for further precipitation of the precipitated aragonite particles.

5. U.S. Patent No. 4,018,877 (M. C. Bennett et al.) describes a continuous process for the production of a particulate precipitated aragonite by carbonating aqueous calcium hydroxide slurry in sucrose solutions. However, due to the cost of the sucrose, the solution had to be recycled and detrimental materials had to be removed by anion exchange resin. The preferred temperature range was between 60°C and 90°C; the pH values were in the range between 7 and 9; and the concentration of the calcium hydroxide was quite low - in the range between one-half and one-twentieth molar.

6. U.S. Patent No 4,018,877 (R. D. A. Woode) describes carbonation of calcium hydroxide slurry, wherein a complexing agent for Ca^{++} is added to the suspension in the gas absorber, after the calcium carbonate primary nucleation stage and before completion of the carbonation step, the complexing agent being e.g. citric acid, ethylenediamine tetraacetic acid (EDTA), aminotriacetic acid, aminodiacetic acid or a hydroxy polycarboxylic acid. Optionally, long-chain fatty acids or their salts can be added, preferably, after the final carbonation stage.

7. U.S. Patent No. 4,157,379 (J. Arika et al.) describes the production of a chain-structured precipitated calcium carbonate by the carbonation of calcium hydroxide suspended in water in the presence of chelating agents, such as aliphatic carboxylic acids, and water-soluble metal salts.

8. U.S. Patent No. 4,157,379 (H. Shibazaki et al.) describes a multi-stage production process for producing a particulate precipitated aragonite, using aqueous calcium hydroxide slurry and carbon dioxide gas or a carbon dioxide containing gas, in the presence of phosphoric acids and water-soluble salts thereof.

9. U.S. Patent No. 4,420,341(T. H. Feringo) describes inorganic fillers (including calcium carbonate) surface modified with carboxylic acids, antioxidants and high-boiling non-reactive liquid agents.

10. JP Patent Publication No. 63260815 (H. Shibata et al.) describes the production of a particulate precipitated aragonite, by reacting carbon dioxide gas with an aqueous calcium hydroxide slurry in presence of phosphoric acid, a phosphoric acid compound, a barium compound and a strontium compound.

11. JP Patent No. 1261225 (H. Shibata et al.) describes reacting carbon dioxide gas with an aqueous calcium hydroxide slurry, in order to produce a particulate precipitated aragonite, which is stated to have improved properties compared with particulate precipitated calcite.

12. U.S. Patent No. 4,824,654 (Y. Ota et al.) describes a process for producing precipitated needle-shaped (5-100 μm) particulate precipitated aragonite, in which a relatively dilute aqueous calcium hydroxide solution (0.04-0.17 wt.%) and carbon dioxide gas or a carbon dioxide-containing gas are reacted together at a temperature of not less than 60°C, in a continuous or semi-continuous (intermittent) manner.[That can be said about the entire relevant prior art]

13. U.S. Patent No. 5,043,017 (J. D. Passaratti) describes a process for producing acid-stabilized precipitated calcium carbonate particles.

14. U.S. Patent No. 5,164,172 (H. Katayama et al.) describes a process for producing a particulate precipitated aragonite, in which a mixture of aqueous calcium hydroxide slurry, aragonite calcium carbonate particles and a

water-soluble phosphoric acid compound are premixed prior to the addition of carbon dioxide gas.

15. U.S. Patent No. 5,342,600 (I. S. Bleakley et al.) describe a process of producing particulate precipitated calcium carbonate, in which aqueous calcium hydroxide slurries of varying concentrations are reacted with carbon dioxide-containing gas under a controlled mixing speed. It is recommended therein to prepare the aqueous calcium hydroxide suspension under high shear mixing and subsequently to lower the energy and shear agitation in the reaction mixture in which the precipitated calcium carbonate particles are formed.

16. U.S. Patent No. 5,376,343 (P. M. Fouche) describes a process for producing various forms of particulate PCC. In the case of aragonite, a mixture of quite dilute aqueous calcium hydroxide solution and a water-soluble source of specific anions (e.g. ammonium nitrate) are premixed prior to addition of CO_2 gas.

17. U.S. Patent No. 5,380,361 (R. A. Gill) describes *inter alia* calcium carbonate particles coated with C12-C22 fatty acids salts.

18. U.S. Patent No. 5,593,489 (K-T. Wu) describes a process for producing acid-resistant calcium carbonate particles for making neutral to weakly acid paper.

19. U.S. Patent No. 5,833,747 (I. S. Bleakley et al.) describes a process for producing a particulate precipitated aragonite, in which an aqueous calcium hydroxide slurry (148g $Ca(OH)_2$ per liter of suspension) is reacted with carbon dioxide gas at an exceptionally slow rate of 0.0026 moles per minute per mole of $Ca(OH)_2$ in a batch operation.

20. WO 9852870 (B. Jackson et al.) describes a multi-stage commercial process for producing a particulate precipitated aragonite, using coarse-grained precipitated aragonite particles as a seeding material. Though the process is claimed to be industrially applicable, it is quite slow and thus of very limited economical value.

21. U.S. Patent No. 5,833,747 (J. W. Bunger et al.) describes a process for producing a particulate precipitated aragonite, in which an aqueous calcium hydroxide solution is reacted with CO_2 gas in a plug-flow reaction system.

22. U.S. Patent No. 5,846,382 (A. von Raven) describes a process for producing inorganic fillers and pigments, including particulate calcium carbonate, of improved whiteness, brightness and chromaticity.

23. U.S. Patent No. 5,861,209 (W. J. Haskins et al.) describes a process for producing a particulate precipitated aragonite, for printing, in which an aqueous calcium hydroxide slurry is first mixed with precipitated aragonite particles for seeding and then it is reacted quite slowly with carbon dioxide gas in a batch operation. After dewatering the product to a cake containing about 70% solids, it is mixed with a typical dispersant, e.g. sodium polyacrylate, and it is further dispersed. This patent discloses the use of mixtures of a particulate precipitated aragonite, with TiO_2 and other inorganic fillers, pigments and flame retardants.

24. U.S. Patent No. 5,939,036 (A. L. Porter et al.) describes a process for producing a particulate precipitated aragonite, in which aqueous mixtures of organic compounds and acids (e.g. ethanolamine and HCl) are used to dissolve impure CaO and to form a calcium hydroxide mixture, which is then reacted with carbon dioxide gas to yield various forms of PCC, depending on the temperature. Controlling the temperature of the carbonation at about 95°C leads to aragonite.

25. U.S. Patent No. 6,022,517 (G. H. Fairchild et al.) describes a process for producing mixtures of precipitated acicular calcite and acicular aragonite particles in the ratio of 75:25 to 25:75, by reacting carbon dioxide gas or a carbon dioxide containing gas and aqueous calcium hydroxide in the presence of a water soluble aluminum compound, by controlling the specific conductivity in a range > 4.0 and up to about 7.0, milliSiemens/cm, at a reaction temperature of from 25-60°C.

26. Pigment Handbook (Vol. I-III; Edited by T. C. Patton; John Wiley & Sons, New York (1973)) describes the properties, the production processes and various uses of aragonite calcium carbonate pigment (c.f. Vol. I; Pages 119-128), as well as those of other pigments that compete in the same market like titanium dioxide, kaolin, GCC, etc. The discussion concerning the influence of the film porosity on the hiding power or opacity of a coating film (c. f. Vol. III; Pages 203-217 and especially on Page 212) may help in understanding some aspects of the present invention.

The entire contents of the above-cited literature, including patents and patent publications, are incorporated herein by reference. It is apparent from the state of the art that known processes for the industrial production of substantially pure particulate precipitated aragonite (>90 parts aragonite: <10 parts calcite), by reacting aqueous calcium hydroxide slurries with carbon dioxide gas or a carbon dioxide containing gas, exhibit serious drawbacks that affect the quality and cost of the final product, as follows:

A. Some of the processes are conducted in aqueous solutions of extremely low concentrations of calcium hydroxide. In some cases it is specified that clear solutions, which contain less than 1 wt.% calcium hydroxide, should be used.

B. In those processes which allow use of aqueous calcium hydroxide slurries, the production rates are very slow and difficult to control.

C. To increase somewhat the rates of production in processes of A and B, the prior art recommends seeding with previously produced aragonite particles. However, this complicates the production processes, especially those operated continuously, and which are otherwise of great commercial potential.

D. Dewatering of particulate precipitated aragonite obtained according to the known art gives rise to relatively wet filter cakes of which the water content is not below 30% and which may thus require a very expensive subsequent drying step.

E. Particulate precipitated aragonite of the prior art requires extensive grinding operations to optimize its particle size distribution (PSD) in order to meet the effective PSD in the range between 0.2μm and 0.4μm, mentioned above. Moreover, the grinding operation tends to contaminate the product, due to attrition of the grinding media, unless very expensive materials of construction are used for this purpose.

F. The known particulate precipitated aragonite is of limited whiteness, mainly due to the high residual impurities in the $CaCO_3/CaO$ feedstock, which it is quite difficult to remove thoroughly, on the industrial scale. Also, the low whiteness of the product is a limiting factor in choosing the suitable sources of its raw materials ($CaCO_3/CaO$).

G. Particulate precipitated aragonite frequently requires one or more post-manufacturing treatment step(s), in order to ensure that the particle surface is hydrophobic, by coating with suitable long-chain carboxylic acids and/or other materials such as silicon greases, e.g. for efficient dispersal in hydrophobic media such as rubber or plastics, and/or to ensure resistance to acidic environments for use e.g. in the paper industry and in the coating industry.

H. Efforts in the prior art to increase the effective refractive index of particulate precipitated aragonite has not so far succeeded in making this material a serious competitor to titanium dioxide.

Accordingly, it is an object of the present invention to overcome all or most of the problems encountered in the prior art, as mentioned in paragraphs A-H, above.

It is an object of the present invention to provide particulate precipitated aragonite, as stated in the preceding paragraph, by a process which is more efficient and less expensive, than those available in the prior art.

It is yet a further object of the present invention to effect such a more efficient and less expensive process as stated in the preceding paragraph, using sources of $CaCO_3/CaO$, which are presently not suitable raw materials for use as e.g. fillers, extenders and pigments, and for other applications, in all of which uses require pigments of high optical properties and high performance, whereby production costs are lowered.

Still another object of the present invention is to provide a particulate precipitated aragonite of a superior quality as stated above, in which the produced particles are treated *in situ* with a hydrophobic agent in order to avoid an extra downstream step and to fine-tune their properties to meet the requirements of the rubber, plastics, coatings (especially durable paints in acidic environments), inks and paper industries (especially paper production in weakly acidic media), an effect of said *in situ* treatment being lowering of production costs.

Still another object of the present invention is to carry out the above-stated more efficient and less expensive process, in a manner which gives rise to filter

cakes which are relatively dry, e.g. with no more than about 20 wt.% water, right after the dewatering stage, and thus additionally lowering production costs.

Another object of the invention is to effect the above-stated more efficient and less expensive process, in such a manner that the produced particulate precipitated aragonite does not require, for most applications, any downstream grinding operations, except for the regular mixing systems which are in any event usually installed in the industries mentioned above, and thus additionally lowering production costs.

Most of all, it is a particular object of the present invention to provide a particulate precipitated aragonite of a better quality than that obtained in the prior art, and especially having a higher whiteness, a lower specific gravity and a higher effective refractive index.

Other objects of the invention will appear from the description which follows.

SUMMARY OF THE INVENTION

It has been surprisingly found in accordance with the present invention, that an industrially viable particulate precipitated aragonite calcium carbonate, which is characterized by its high whiteness, high effective refractive index, and especially by its low specific gravity (below 2.5 g/cm^3), can be produced, and that the above-mentioned objects of the present invention can be achieved, by a process which comprises reacting an aqueous calcium hydroxide slurry with a gas selected from carbon dioxide and a gas containing it, wherein the parameters of the process, including e.g. at least one preselected active agent, modes of operation, operating concentrations of raw materials, operating temperatures, operating pH range and high shear mixing speeds, are strictly controlled such that the desired product is obtained. In a particular embodiment, flotation of the product occurs during such process.

The process of the invention for producing a particulate precipitated aragonite in accordance with the invention, is preferably further characterized by at least one, and preferably all, of the following features: (a) the active agent comprises at least one member selected from the group consisting of carboxylic acids of formula $CH_3(CH_2)_nCOOH$, where n is 7-9, and their carboxylate salts, esters, anhydrides, and acyl halides, and ketenes of formula $CH_3(CH_2)_{n-1}C=C=O$; (b) the concentration of the active agent is within the range of between 0.2 wt.% and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate; (c) the slurry contains calcium hydroxide in a concentration within the range of from 3 to 30 wt.%, more preferably 4 to 20 wt.%; (d) the product is produced at a pH between 8 and 11, preferably between 9 and 10; (e) the process is effected at a temperature in the range between 60°C, desirably between 80°C, and the boiling temperature of the reaction mixture; (f) the process is effected either in a semi-continuous (intermittent) mode of operation, or more preferably in a continuous manner; (g) the process is effected under high shear mixing e.g. with a mixer comprising a rotor/stator or a rotor only, the mixer peripheral (tip) speed being preferably at least 5 m/sec. In a particular embodiment, this process is effected in a continuous mode of operation under high

shear mixing with a mixer comprising a rotor/stator or a rotor only, at a temperature in the range between 90°C and the boiling temperature of the reaction mixture, the active agent - preferably present in an amount in the range between 0.2% and 10 wt.%, calculated on the weight of calcium carbonate - being selected from the carboxylic acids and their calcium salts, and the slurry contains calcium hydroxide in a concentration within the range of from 5 to 15 wt.%, the active agent being desirably premixed with the calcium hydroxide slurry prior to reaction with carbon dioxide.

The present invention also provides as a novel chemical substance - which is of course obtainable in accordance with the present process, a particulate precipitated aragonite, which has a specific gravity of <2.5 g/cm^3 (preferably <2.3 g/cm^3, more preferably <2.0 g/cm^3, even more preferably <1.8 g/cm^3) after drying at 120°C, and a specific gravity <2.5 g/cm^3 after ignition for eight hours at 500°C. In a particular embodiment, the product has a specific gravity of <2.3 g/cm^3 after drying at 120°C, and a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500°C.

.A typical such product may be further characterized by at least one of the following features: it contains said carboxylate calcium salt(s) in an amount between 0.2 and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate; it has a specific gravity <2.2 g/cm^3, preferably <2.0 g/cm^3, more preferably <1.8 g/cm^3; a product previously dried at 120°C for 12 hours has a loss on drying at 300°C for 8 hours of <10% wt.%, based on the weight of calcium carbonate; a product previously dried at 120°C for 12 hours has a loss on ignition at 500°C for 8 hours of <10% wt.%, based on the weight of calcium carbonate; after drying at 120°C for 12 hours, and/or drying for 8 hours at 300°C, and/or firing for 8 hours at 500°C, it still has a specific gravity < 2.5 g/cm^3.

The product of the present invention can be used as a thickening material, a filler, an extender and particularly as a pigment for the pharmaceuticals, plastics, adhesives, printing, coating (paint), paper, rubber, filtration, and many other industries.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic flow sheet for production of particulate precipitated calcium carbonate according to the prior art.

Figure 2 shows a schematic flow sheet for production of a particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 3 shows in schematic vertical section, a reactor/flotation cell for producing a particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 4 shows a SEM picture of a particulate precipitated aragonite, in accordance with an embodiment of the present invention.

Figure 5 shows an XRD spectrum of a particulate precipitated aragonite, in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the process of the present invention, a slurry of calcium hydroxide in water and carbon dioxide gas or a carbon dioxide containing gas are reacted together in the presence of the active agent under stringent process conditions, to generate a particulate precipitated aragonite having unique properties.

The product of the present invention is characterized by its low production cost and by its unique physical properties (high whiteness, high effective refractive index and low specific gravity (<2.5g/cm^3)) and by its excellent chemical properties (hydrophobicity and resistance to weak acids), which make it particularly suitable as a thickening material, a filler, an extender and most of all as a pigment for the printing, coating (paint), paper, rubber, plastics, filtration, adhesives, pharmaceuticals and other industries.

As stated above, Fig. 1 shows a flow sheet for production of particulate precipitated calcium carbonate according to the prior art. By contrast, in order to define the most suitable conditions to operate the carbonation stage of the present invention, a detailed description of parameters for the present process is given below. These also include some details of how to operate the upstream and

downstream stages of the carbonation stage, as these may affect the final outcome (c. f. Figs. 2 and 3).

In Figure 1, which is a schematic representation of a prior art procedure for making a precipitated calcium carbonate, quicklime (CaO) and water which react together giving slaked lime are fed to reactor 20 via respective conduits 1 and 2, and optional additives such as aragonite calcium carbonate particles for seeding, phosphoric acids and salts, chelating agents, dispersants, and surface active agents, may also be added at this stage via conduit 3. The initial product "milk of lime" (calcium hydroxide) is fed via filter or hydrocyclone 4 (large solid particles being removed at 12) into carbonator 22, to which there is also fed gaseous carbon dioxide (or a gas containing it) via conduit 5 and the aforementioned optional additives via conduit 6. The reaction product including any contaminants exits carbonator 22 as an underflow via conduit 7 and/or an overflow via conduit 8, to further operations (at site 24) such as dewatering, grinding and coating; for such further operations there may be added optionally via conduit 9, e.g. dispersants, surface active agents, greases, silicon greases, long-chain carboxylic acids and their salts, inorganic pigments, and/or dyeing agents. The filtrate and water vapors exit the system via conduit(s) 10, while the final product (which may be wet or dry and optionally post-treated) exits via conduit 11.

In Figure 2, which is a schematic representation of a procedure for making a particulate precipitated aragonite in accordance with the present invention, quicklime (CaO) and water which react together giving slaked lime are fed to reactor 30 via respective conduits 1 and 2, and the present active agent (and optionally also additives such as phosphoric acids and salts, chelating agents, dispersants, and surface active agents) may be added at this stage via conduit 13. The initial product "milk of lime" (calcium hydroxide) together with active agent if added to 30 (and optional additives) is fed via filter or hydrocyclone 14 (large solid particles being removed at 12) into carbonator 32, to which there is also fed gaseous carbon dioxide (or a gas containing it) via conduit 5 and the active agent (and possibly the aforementioned optional additives) via conduit 16. It will be appreciated that the active agent may be added either to reactor 30 or to carbonator 32, or to both.

Contaminants and liquid exit carbonator 32 as an underflow via conduit 7, whereas - owing to the fact that an embodiment of the present process includes simultaneous flotation - the desired product exits as an overflow via conduit 18, to further operations (at site 34) such as dewatering, grinding and coating; for such further operations there may be added optionally via conduit 19, e.g. dispersants, surface active agents, greases, silicon greases, long-chain carboxylic acids and their salts (including if desired those within the definition of the present active agents), inorganic pigments, and/or dyeing agents. The filtrate and water vapors exit the system via conduit(s) 10, while the final product (which may be wet or dry and optionally post-treated) exits via conduit 11.

Slaking of quicklime

Though this operation is well known in the prior art, it is worthwhile to choose a preferred mode of operation which is best adapted to the process of the present invention. Thus, fresh slaked lime is preferably prepared in a continuous mode of operation, which enables operation of the downstream carbonation stage using low inventories and exploiting to its maximum the energy that is liberated in the reaction between the water and the CaO, before this precious energy is lost to the surroundings. The present invention desirably makes use of this energy to effect the step of carbonation of the aqueous calcium hydroxide slurry at relatively high temperatures, more preferably without cooling or heating, or in other words, without adding or subtracting energy, and thus utilizing only the energy liberated by the cabonation reaction together with the energy produced by a powerful mixing system. Once again, use of fresh and still warm milk of lime is preferably an important factor in the success of the carbonation stage and this is more preferably effected, as mentioned above, in a continuous mode of operation, the temperature of the slaked lime being preferably maintained at somewhat below the temperature of the carbonation stage. However, in the alternative, a batch mode of operation may also be used for process of the present invention.

Mixing of quicklime

In some prior art patents it is recommended to use high shear mixers to slake the CaO with water. The process of the present invention is quite tolerant to the kind of mixing, as long as the slaking reaction is complete and the maximum energy is liberated. Mixers that comprise rotor/stator mixing systems and mixers that comprise rotors only are suitable.

Purification of slaked lime prior to carbonation

There are numerous methods of purifying slaked lime before its utilization in the carbonation stage. Filters to remove large insoluble particles and/or separation of these particles by hydrocyclones are two efficient methods for this purpose. Usually, particles of greater diameter than 40 μm (up to 70 μm) are removed prior to the carbonation stage and the coarse particles can then be discarded or used in the construction industry, for example. The fine slurry is then ready for carbonation in the subsequent downstream stage.

Sources of $CaCO_3/CaO$:

Many sources of $CaCO_3/CaO$ are too contaminated to be used to produce by known methods, a particulate precipitated aragonite for the printing, coating (paint), paper, rubber, plastics, filtration, glue, pharmacy and other industries and their main use is, as very inexpensive materials, in the construction industry. On the other hand, the present invention may allow utilizing many of these "impure" $CaCO_3/CaO$ sources and turning them into a particulate precipitated aragonite, of filler, extender and pigment grades. The present invention, as is manifested in the carbonation stage, is superior over any state of the art technology in salvaging $CaCO_3$ mines and turning them to profitable use, without changing greatly the state of the art methods for preparing the slaked lime.

Use of Additives

The state of the art technology for slaking quicklime includes adding a variety of additives into the milk of lime prior to the carbonation stage. According to

the present invention, one of the preferred modes of operation is to add the active agent into the milk of lime prior to the carbonation reaction. Those skilled in the art of producing precipitated calcium carbonate must carefully check that the other additives, if any are present in the milk of lime, do not interfere with the ability of the active agent to enhance formation of particulate precipitated aragonite and to cause its flotation in the carbonation reactor. For instance, the use of 1 wt.% (based on the calcium carbonate) of phthalic acid or trimellitic acid with about 1 wt.% (based on the calcium carbonate) of the active agent, cause the formation of particulate calcite in the carbonation stage, instead of aragonite. In other cases, the additives may cause the formation of mixtures of particulate precipitated calcite and aragonite.

The Reaction/Carbonation Stage

This operation is well known in the prior art. However, as this stage is the essence of the present invention, it is worthwhile to choose the mode of operation that suits it best. For example, although the use of aragonite particles for seeding is a recommended procedure in the prior art, it seems at the present time that this practice is unlikely to have any particular utility in the process of the present invention, since use of the active agent enables all desired objectives to be achieved.

As the most important functions of the active agent in the present invention are to catalyze the production of particulate precipitated aragonite, to cause its flotation in the carbonation reactor and to improve the physical and chemical properties of the resulting product, all necessary measures should be taken in order to maximize these functions.

The Nature of the Active Agent and its Origin

While the scope of the present invention is not to be regarded as limited by any theory, nevertheless it may be likely that the calcium salts of the carboxylic acids of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7, 8, and 9 (or mixtures thereof), operate in practice as the functioning active agent in the present process.

It should not be ruled out, however, that for example, other derivatives of such acids within the scope of the invention may participate in similar activity.

The above-mentioned calcium salts of the relevant acids may be used as raw materials in the present invention. However, other compounds, which undergo chemical transformations to form the active agent under the process conditions, also serve this purpose as raw materials in the production of the desired particulate precipitated aragonite.

In a particular embodiment of the invention, the active agent is selected from carboxylic acids of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7, 8, or 9, and including mixtures thereof. All three acids can be quite easily introduced into any of the production facilities. Pumping of these acids when their temperature is held above their melting points (e.g. >60°C) seems to be a very useful method to deliver the acids into the suitable production units. Under such conditions, these thermally stable acids are immediately converted into their respective calcium salts when they are mixed with the hot aqueous calcium hydroxide slurry or with the hot carbonation mixture at pH>7. As water is the only by-product of the reaction between the calcium hydroxide and the respective acids, the use of these acids, as raw materials in the process of the present invention, seems to have no harmful side effect.

The respective acid anhydrides of the general formula: $(CH_3(CH_2)_nCO)_2O$, including mixtures thereof, where n = 7, 8, and 9, are as good a source for the active agent, as the corresponding acids. However, the anhydrides are much less safe to handle and they are much more expensive than the respective acids.

The carboxylate salts of the acids of the general formula: $CH_3(CH_2)_nCOOH$, including mixtures thereof, where n = 7, 8, and 9, can serve as raw materials in the process of the present invention, e.g. where the cations are selected from Na^+, K^+, NH_4^+, Li^+, Mg^{++} and especially Ca^{++}, but, generally, the use of these salts does not appear to have any advantage over the free acids. On the contrary, the salts are more expensive, they are not as easy to handle on an industrial scale as the respective acids and, except the Ca^{++} salts, all the other salts add cations that, so

far as is presently known, are not required in the present process. The Mg^{++} salts present a special case, as they leads to the formation of hydromagnesite and thereby to a dramatic rise of the surface area of the product, to its contamination and to a large increase in the water content in the wet filter cake. Therefore, in the process of the present invention only limited concentrations of this cation are desired, i.e. <3 wt.%, based on the calcium hydroxide.

Esters of the following general formula: $CH_3(CH_2)_nCOOR$, where n = 7, 8, and 9 and R is an esterification radical such as alkyl, e.g. CH_3, C_2H_5, C_3H_7, etc., are also suitable candidates for the active agent in the present invention. However, in order for these compounds to generate e.g. the corresponding calcium salts, they have to undergo a basic hydrolysis, which may preferably be done by premixing them in the hot and basic aqueous calcium hydroxide slurry, in which they are hydrolyzed and thus converted to the respective Ca^{++} salts. However, the use of these esters in the process of the invention appears to be inferior to the use of the respective acids, for reasons which will be self-evident to the skilled person.

Chemically equivalent to the other preferred active agents specifically mentioned above, are ketenes of the general formula: $CH_3(CH_2)_{n-1}C=C=O$, wherein n = 7, 8, and 9, and including mixtures thereof, behave in a similar manner and entail similar drawbacks, as for the acid anhydrides, as mentioned above.

Therefore, the acids of the general formula: $CH_3(CH_2)_nCOOH$, wherein n = 7, 8 and 9, including mixtures thereof, are the presently preferred source for the active agent to be used in the process of the present invention. More specifically, decanoic acid (wherein n=8) is the presently preferred acid, since it is the least expensive in this series of active carboxylic acids and it is located at the middle of the range of these active acids having n=7, 8 and 9.

The Reactor/Carbonator/Flotation Cell

As already mentioned above, the carbonation stage can be conducted in any well-stirred reactor according to the prior art. However, due to the fact that the

active agent is a unique material that can enhance the formation of particulate precipitated aragonite, in the reaction between aqueous calcium hydroxide slurries and carbon dioxide gas or a carbon dioxide containing gas, and also due to the fact that the active agent can cause this product to float, the presently preferred carbonators to be used in the process of the present invention are flotation cells.

These cells may be operated somewhat differently from the regular carbonators and the regular flotation cells, as both functions (carbonation and flotation) take place in the same production unit for particulate precipitated aragonite of the present invention. The exact set-up of these flotation cells can vary, as this will depend on, for example, the preferences of the skilled designer, the precise nature of the desired product, the quality of the aqueous calcium hydroxide slurries, etc. For example, a flotation cell like that depicted in Fig. 3, containing stator/rotor or rotor only S, is suitable for carrying out the inventive process, and of which the main features are as follows:

A. The stream of slaked lime (14) is preferably introduced near the inner circumference of the reactor and above the stirring blades.

B. The stream (5) of carbon dioxide gas or carbon dioxide containing gas is preferably introduced through suitable spargers at a point below the stirring blades, but still not too close to the bottom of the cell, to avoid excessive mixing near the outlet stream (7) of the contaminants and liquid.

C. The wet product and the gas are preferably discharged from the top (18) of the cell. The customary skimmer for skimming the product out of the flotation cell, and hydrocyclones for efficient product/gas separation, are not shown in Fig. 3.

Mode of Operation in the Carbonation Step

Continuous reaction/carbonation of the aqueous calcium hydroxide slurry with carbon dioxide gas or a carbon dioxide containing gas is the most suitable mode of operation for the present invention, especially because of the huge potential market for the produced particulate precipitated aragonite.

Semi-continuous (intermittent) operations may also be used. However, as may be understood from the desirability of operating the process at its utmost

efficiency, e.g. as a flotation operation, it is unlikely that an intermittent mode of operation can compete economically with the continuous mode of operation.

A "real" batch mode of operation, in which the milk of lime and the active agent are mixed together and carbon dioxide gas or a carbon dioxide containing gas is introduced to precipitate the desired product until the reaction mixture turns neutral (at about pH~7), appears not to be viable, probably because the active agent is not efficient in catalyzing the formation of particulate precipitated aragonite, at the high initial pH characteristic of the batch mode of operation in this case, and/or because the active agent is adsorbed onto the surface of the first formed crystals of particulate precipitated aragonite, where it is then "buried" under the subsequent precipitated calcium carbonate. In such circumstances, the active agent is very quickly depleted from the reaction mixture, and the process of the invention, as such, is likely to become inoperable.

Temperature of the Carbonation Step

The prior art teaches producing a particulate precipitated aragonite, at a temperature range between 60°C and the boiling temperature of the reaction mixture, at ambient pressure, and the present process is preferably conducted similarly, because lower temperatures favor the formation of calcite.

On the other hand, operating the process at a temperature as close as possible to the boiling point of the reaction mixture is presently particularly preferred, since these conditions give a product of relatively lower water content in the wet filter cake, which is a great advantage in many applications of the product.

While the present process may be operated at higher temperatures and pressures (since the active agent is stable under such conditions), this kind of operation is associated with serious technological problems that may adversely affect the whole economics of the process.

Concentration of $Ca(OH)_2$ slurry in the Carbonation Step

The prior art method for producing a particulate precipitated aragonite, may be classified into three principle modes of operation. The first mode is operated at

very low concentrations of the calcium hydroxide in water, and in some cases a clear solution of <1 wt.% calcium hydroxide is used. In the second mode, there are used aqueous calcium hydroxide slurries and active agents to induce the formation of the desired particulate precipitated aragonite, albeit, at very low production rates. In the third mode, particulate precipitated aragonite is used for seeding, in order to improve production rates.

The present invention requires relatively high concentrations in the aqueous calcium hydroxide slurries and the production rates are very fast. Actually, at the range of very low concentrations of <3 wt.% (based on the calcium hydroxide) the present process may not "ignite" right away and under these circumstances, only precipitated calcite calcium carbonate particles may be obtained.

The present invention can use quite dense aqueous calcium hydroxide slurries of up to about 30 wt.% calcium hydroxide, but such dense slurries are very viscous and are very difficult to handle. Therefore, the preferred range of concentrations of the aqueous calcium hydroxide slurries, according to the present invention, are in the range between 4% and 20 wt.%, and more preferably between 5% and 15 wt.% calcium hydroxide. In these ranges, the viscosity of the reaction mixture permits smooth operation, while the energy maintained already in the feed of aqueous calcium hydroxide slurry (as discussed above), plus the energy liberated by the carbonation reaction, as well as the energy liberated by the mixing system, are sufficient to maintain the desired reaction temperature without any external heating or cooling.

Concentration of Active Agent in the Carbonation Step

To simplify the calculations of how much active agent is needed in the process and how much of it may be included in the product of the present invention, we prefer to use the weights of the respective acids, since the carboxylate moieties differ from their respective acids by less than 1%. Therefore, in cases that suitable ketenes, esters, carboxylate salts, acid anhydrides and/or acyl halides are being used, the equivalent weight of the respective acid should be calculated, unless otherwise indicated. Moreover, as we are presently not aware of

differences among the activities of the acids of the general formula $CH_3(CH_2)_nCOOH$, wherein n = 7, 8, and 9, including mixtures thereof, their individual contribution to the total weight of the active agent should be calculated arithmetically, namely by adding the weight of each individual acid, as if these are of the same chemical entity. This concept is important for understanding this invention and particularly the claims, unambiguously. The difference between the molecular weights of the respective acids (~±10%) is not a great problem, because a person skilled in the art will in any event operate the process in a manner which is not sensitive to even larger variations of the concentrations of the active agent, namely, of >±10 wt.%, based on $CaCO_3$. Moreover, when using decanoic acid as the presently preferred active agent, the present invention will not even be subject to the above-mentioned inaccuracy.

To determine the concentration range of the active agent in the present invention, it is important to be aware of the various functions of this agent in the production process and the effects that it produces in the final product.

The prior art describes many additives that assist in producing particulate precipitated aragonite, but none of these additives is comparable to the present active agent for the following two major reasons:

1. The active agent leads to a dramatic reduction of the specific gravity of the particulate product and allows use of the flotation method to separate the "light" particulate precipitated aragonite, from the "heavy" contaminants (containing aluminosilicates and heavy metal salts, carbonates and oxides). These "heavy" particles sink down to the bottom of the carbonator/flotation cell and are discharged from the production unit without reaching the downstream filter, and
2. The optical properties of the particulate precipitated aragonite product are altered and its effective refractive index is increased dramatically.

Thus, the pure product of the present invention, on the flotation embodiment, is being carried to the top of the reactor/carbonator/flotation cell, by the small bubbles that adhere to the tiny precipitated aragonite particles, and this relatively pure product is discharged from the top of the carbonator/flotation cell prior to any downstream operation. Thus, in this embodiment, the present process

entails an intrinsic, built-in, extra purification operation, prior to the downstream dewatering operation, which is not so common in the prior art.

This unique property of the active agent to cause the flotation of the "light" particulate precipitated aragonite, is also a reason why this embodiment of the present invention is superior over any of the prior art production technologies in exploiting highly contaminated sources of $CaCO_3/CaO$, which have hitherto been unsuitable as raw materials for production of a particulate precipitated aragonite, of filler, extender and pigment quality grades. Such sources can now be utilized successfully, using this novel technology of the present invention.

Since the aqueous calcium hydroxide slurry is usually quite contaminated and the impurities are liable to affect performance of the active agent, the threshold (minimum) concentration of the active agent will vary, but is within the competence of a skilled person to determine, under any particular set of circumstances. In any case, it is desirable to avoid this threshold concentration at the carbonation stage, as this is a point of instability and would involve unnecessary risk to the desired objective. When considering use of a new feedstock of $CaCO_3/CaO$, laboratory experiments will reveal the minimum concentration of the active agent, which is necessary to start the production of particulate precipitated aragonite, without any faults (vis-a-vis the pertinent $CaCO_3/CaO$ feedstock). This value is expected to be in most cases above 0.2 wt.%, preferably within the range 0.4% to 3 wt.%, based on the calcium carbonate.

It is very important to note that this threshold concentration, discussed above, for catalyzing the production of particulate precipitated aragonite of the present invention (~0.2% wt.%, based on $CaCO_3$) is substantially above the threshold concentration that is required to cause the flotation of this product in aqueous solutions (~0.02% wt.%, based on $CaCO_3$) and that by operating in the concentration range merely for a "proper" flotation process, nothing that is disclosed in the present invention really happens. Actually, the optimal physical and chemical properties of the particulate precipitated aragonite calcium carbonate of the present invention are attained at above 100 fold of this concentration (~2-3 wt.%, based on $CaCO_3$).

Other factors may indicate use of even higher concentrations of the active agent in the production process of the present invention. For instance, coating the surface of the particulate precipitated aragonite, with a predetermined rather thick layer of the active agent, *in situ*, in a carbonator/flotation cell, may require quite high concentrations of this material, which may exceed 5%, 10% and even 15 wt.%, based on $CaCO_3$, in order to produce good surface coated hydrophobic and acid resistant particulate precipitated aragonite (e.g. for master batches). Naturally, at such high active agent concentrations, the cost component of the coating should then be compared to the alternative possibilities of downstream coating, which are also available in the prior art, as well as in the present invention (c.f. figs. 1 and 2, respectively). Another serious reason to avoid operating the process at too low concentrations, is the fact that the chemical and physical properties of the product, and especially its optical properties and specific gravity (which may well be interdependent), are dramatically affected by the concentration of the active agent.

In between the upper limit and the threshold limit of the concentration of the active agent in the process of the present invention, the optimum concentration should also be determined by one skilled in this art, either vis-a-vis the quality of the $CaCO_3/CaO$, or whenever the properties of the product are to be changed. The active agent is not an expensive material, but still it may throw an economical burden on the total cost of the final product due to the fact that particulate precipitated aragonite is a relatively inexpensive material.

Intuitively, the concentration of 10 wt.%, based on the calcium carbonate, seems to be an economical upper limit of the active agent, while 0.2 wt.%, wt; based on the $CaCO_3$, seems to be its threshold (minimum) concentration.

Carbon Dioxide in the Carbonation Step

Use of carbon dioxide gas or a carbon dioxide containing gas is well known in the prior art methods for producing precipitated calcium carbonate particles. The process of the present invention is similar in this respect to the prior art processes that operate with substantially pure carbon dioxide gas as well as with mixtures of carbon dioxide with up to about 90 wt.% inert gases (e.g. air). At lower

concentrations of the carbon dioxide in the gas (<10 wt.%), however, the efficiency of the process may be too low.

Additives in the Process:

The process of the present invention is quite self-sufficient and requires only the active agent in suitable quantities, as discussed above. The active agent can be introduced preferably already premixed with the aqueous calcium hydroxide slurry, or alternatively (or additionally) it can be introduced directly into the carbonator. The active agent can also be used downstream the carbonation stage, but that, naturally, has no effect on the production of particulate precipitated aragonite in the carbonator.

It appears that the active agent has a surprising affinity to the aragonite which is unlikely to be adversely affected by the presence of other additives. Consequently, additives like phosphoric acids and water soluble salts thereof, can be used in the present invention to modify the product properties by increasing the aspect ratio of the thus formed acicular crystals; polyacrylates and some short-chain carboxylic acids can be used to modify the rheology of the product mixtures and allow operation at higher calcium hydroxide concentrations and, consequently, at higher throughputs; and chelating agents can be used to convert heavy metals into water-soluble species and once again lead to super-pure particulate precipitated aragonite.

It is nevertheless prudent to check carefully the effect that well known additives of the prior art may have on the action of the active agent, but in most cases the active agent will be the dominant catalyst for the purpose of the present invention and, therefore, such additives can usually be introduced at various stages of the process, as is customary in the prior art (c.f. Figs. 2 and 3).

The Mixing System

The need for high shear mixing in this process is well known in the relevant art. The mixers may be a rotor/stator type or a rotor only type. Usually, the latter one is used to produce relatively larger product particles, while the rotor/stator type leads to much higher attrition of the acicular crystals. On the other hand, the

rotor/stator type may allow a more efficient dispersion of the gas bubbles, thereby improving the quality of the product. The skilled operator will utilize the preferred mixing system for working or enhancing the present process. The type of mixers and the rotor speed should be optimized according to the desired carbonation performance and the desired product characteristics.

The lower limit of the rotor speed (hereinafter - "Tip Speed" or "Peripheral Speed") is known in the prior art. A requirement of a minimum tip speed of about 5m/sec., to effect the formation of desired product is not unusual in this art.

The upper limit of the rotor speed is determined by mixer technology, cost of the specific mixer, the nature of the desired product and the energy that is to be used. For instance, the higher the rotor speed, the lower may be the reaction time (in a continuous process, the reaction time is termed HUT (Hold Up Time) and it is calculated as follows: HUT = V (the carbonator volume) / F (the discharge rate of the product mixture out of the carbonator)). This in turn may lead to small particles. A skilled person in this art will know how to optimize the kind of mixers and rotor speeds above the minimal peripheral speed, which is preferably 5m/sec

<u>The Reaction Duration in the Reactor/Carbonator/Flotation Cell</u>

As already mentioned above, the carbonation step is preferably conducted in a continuous mode of operation. In such a case, "reaction duration" is hardly relevant, but we can calculate the HUT (Hold Up Time), which lies essentially within the range between 5 minutes and 180 minutes. At below the lower limit of the HUT the yields may be too low and the PSD (Particle Size Distribution) of the product may be too small, while at the upper limit of the HUT the yields may be excellent, but the PSD may also be too small, because of excessive attrition of the product in the flotation cell Once again, the skilled person will be able to determine by experiment, suitable working parameters vis-a-vis the desired product properties and to optimize its quality and cost.

The present invention will now be described in more detail by way of Examples, which are presented for illustration purposes only and are not be construed restrictively.

Experimental:

Raw Materials:

A. All raw materials were purchased from Aldrich, unless otherwise specified.

B. Ethyl decanoate was prepared by reacting decanoyl chloride with ethanol in the presence of triethylamine at about 50°C. After about 3 hours the product was washed with water to remove water-soluble residues and it was then dried at about 50°C under a vacuum of about 30 mm/Hg.

C. Sodium decanoate was prepared by thoroughly mixing decanoic acid with 2% aqueous NaOH at about 70°C until the pH passed 10.

D. Potassium decanoate was prepared by thoroughly mixing decanoic acid with 2% aqueous KOH at about 70°C until the pH passed 10.

E. CaO(1) - of Arad, Israel. F. CaO(2) - of Shfeya, Israel.

G. Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.

H. CO_2 - Cylinders of 100 % pure compressed gas of Mifalay Hamzan Ltd., Haifa.

I. The Paint Constituents:

Nopco NDW of Henkel

Cellosize QP 15000 (hydroxy ethyl cellulose) of Union Carbide

Disperse One (45% N.V.) of Tambur, Israel

Synperonic NP10 of ICI

TiO_2 (Kronos 2160) of Kronos (However, similar TiO_2 pigments, like Tioxide R-TC90 and Tioxide TR92, of which their D_{50}= 220 nm ± 20 nm may serve equally well)

Synthetic sodium aluminum silicate (p820) of Degussa

Kaolin clay (D_{50} = 3.1 micron) of Engelhard

$CaCO_3$ powder (d_{50}=3.5 microns) of Polychrom, Israel - "Girulite-8"

Talc (D_{50} = 12.3 micron) of Lusenac Val Chisone

Copolymer vinyl acetate acrylate emulsion (55% N.V.) of Cerafon, Israel

Butyl diglycol acetate of Union Carbide

Kathon LXE of Rohm & Haas

Ammonia (25%) of Frutarom, Israel

Instruments and Accessories:

1. pH meter/controller; Jenco; Model 3671; Made in China.
2. pH electrode; Hanna Industries; type HI 1131B (Glass Probe).
3. Thermometer; Jenco Model 3671; Made in China.
4. Peristaltic pump; Watson-Marlow; Model 505u (variable speed).
5. Agitator; Ika; Model RW-20 (variable speed).
6. Dissolver; Hsiangtai; Model HD-550; Made in Taiwan
7. Ultra-turrax® T50; Ika; rotor d = 3.8 cm; stator d = 4 cm.
8. Disk type rotor of d = 12 cm.
9. Disk type rotor of d = 8 cm.
10. Saw-blade type rotor of d = 9 cm.
11. Saw-blade type rotor of d = 4.8 cm.
12. Hydrocyclone 2"; Mozely; P = 50 psi; vortex finder = 11 mm; spigot = 6.4 mm.
13. Vacuum pump; Vacuumbrand GmbH; Model MD 4C.
14. Buchner + filter cloth with 8-10µm pores.
15. XRD (X - Rays Diffractometer); Siemens D-500 for the crystallographic phases.
16. SEM (Scanning Electron Microscope); Jeol 5400 for the shapes of the particles.
17. Colorimeter; Hunterlab D25-PC2 for whiteness measurements.
18. Colorimeter; ACS instrument (Applied Color Systems).
19. Ultrasonic bath (10 l); Selecta, Spain - "ULTRASONS".
20. Analytical Balance; Shekel Ltd., Israel.
21. HPLC Analyzer; Waters HPLC Analyzer (Detector 486 + Autosampler 717 + Pump 510 + millenium Software).
22. HPLC Column; Phenomenex C18(250 mm x 4.3 mm; 5µm Particle size).

PREPARATION I - Preparation of Aqueous Calcium Hydroxide Slurries:

The aqueous calcium hydroxide slurry was prepared in the laboratory in a batch mode of operation as follows: 40 kg of tap water were introduced into a 50 l stainless steel 316 reactor that was equipped with a steam heated jacket, a thermometer and with the Haiangtal Dissolver with a rotor of d = 12 cm. The Dissolver was operated at 200 rpm, 4 kg of CaO (Shfeya) were added to the reactor during less than 10 minutes and the slurry was allowed to stir for 10-60 minutes. At that time the temperature rose to above 60°C and when it reached its maximal temperature at 80-90°C, the mixture was ready for its purification prior to the carbonation stage, as follows:

a. The slurry passed a stainless steel 316 screen to remove particles of d > 2 mm, and

b. The filtered slurry passed a hydrocyclone to remove particles of d > 50 μm.

Notes:

At this point the warm aqueous calcium hydroxide slurry was ready for its use in the carbonation stage and its temperature was maintained at a preset value by heating the slurry in the above reactor in order to control the temperature in the carbonator.

The potential active agent(s) and any optional additives could be blended into the warm slurry at a preset concentration before the purification steps a. and b. or thereafter.

This batch mode of operation is used only in the laboratory tests. The production plant is intended to be operated under a continuous mode of operation, as is discussed herein.

PREPARATION II - Preparation of Aqueous Calcium Hydroxide Slurries:

PREPARATION I was repeated using CaO of Arad, a substantially purer raw material than that of Shfeya (the respective whitenesses are >95% and ~86%).

EXAMPLE 1 - Screening Test for the Potential Active Agents:

Possible active agents were investigated by producing particulate precipitated calcium carbonate according to the following procedure:

2 kg tap water were added to a 3.2 l stainless steel 316 reactor (of inner diameter d = 15 cm and length ~ 18 cm), equipped with a steam heated jacket, a pH electrode, a thermometer and the Hsiangtai Dissolver with a saw-blade rotor of d = 4.8 cm (c.f. Fig 3). The Dissolver was operated at a preset speed and carbon dioxide gas or a carbon dioxide containing gas and the aqueous calcium hydroxide slurry of PREPARATION I, containing already the active agent, were fed simultaneously into the reactor, while maintaining the pH, the temperature and the production rate at preset values. The product was collected at the top of the reactor, and the impurities were discharged from the bottom of the reactor (naturally, the product exited from the bottom of the reactor when the experimental active agent did not lead to a particulate precipitated aragonite and to its flotation).

The first 10 l of resulting slurry were discarded. The residual slurry was collected and it was filtered through a filter-cloth on the Buchner using a vacuum pump to dewater the product. The filter cake was dried for 12 hours at 120°C and the crystallographic morphologies and the shapes of the crystals of the precipitated calcite and/or aragonite calcium carbonate particles were determined using XRD and SEM analyses, respectively. The results are shown in the Table 1, below.

The process set points - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10m/sec.).
2. pH = 9.5.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).
6. Potential active agent concentration = 1 wt.%, based on $CaCO_3$.

Table 1- the results of EXAMPLE 1

Test #	Active Agent	Number of Carbons	Product (Isomorph)
1	Propionic acid	3	Calcite
2	Lactic acid	3	Calcite
3	Pyruvic acid	3	Calcite
4	Acrylic acid	3	Calcite
5	Methoxyacetic acid.	3	Calcite
6	Methacrylic acid.	4	Calcite
7	Butanoic acid	4	Calcite
8	Pentanoic acid	5	Calcite
9	Hexanoic acid	6	Calcite
10	Heptanoic acid	7	Calcite
11	Octanoic acid	8	Calcite
12	Phthalic acid	8	Calcite
13	Terephthalic acid	8	Calcite
14	2-Ethylhexanoic acid	8	Calcite
15	Nonanoic acid	9	Aragonite
16	Nonanoic acid *	9	Aragonite
17	Azeleic acid	9	Calcite
18	Trimelitic acid	9	Calcite
19	Decanoic acid	10	Aragonite
20	Decanoic acid *	10	Aragonite
21	Sodium decanoate	10	Aragonite
22	Potassium decanoate	10	Aragonite
23	Ethyl decanoate	12	Aragonite
24	Decanoyl chloride	10	Aragonite
25	Decanoic acid anhydride	20	Aragonite
26	Undecanoic acid	11	Aragonite
27	Undecanoic acid*	11	Aragonite
28	4-Butylbenzoic acid	11	Calcite
29	Dodecanoic acid	12	Calcite
30	Palmitic acid	16	Calcite
31	Stearic acid	18	Calcite
32	Oleic acid	18	Calcite
33	$MgCl_2$	-	Calcite
34	$AlCl_3$	-	Calcite
35	$C_{12}H_{25}C_6H_4SO_3H$ (LABSA)	18	Calcite

* - Was pumped continuously and directly into the carbonator.

<u>EXAMPLE 2 - a Screening Test for Interfering Compounds:</u>

EXAMPLE 1 was repeated, except that in all the experiments 1% (wt; based on the calcium carbonate) decanoic acid was premixed in the aqueous calcium

hydroxide slurry feed and in each experiment an additional experimental active agent was added to study its effect on the activity of the decanoic acid. The results are shown in Table 2, below.

The process set points' - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.)
2. pH = 9.5. 3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agents concentrations = 1 wt.% decanoic acid + 1 wt.% potential active agent based on $CaCO_3$.

Table 2- the results of EXAMPLE 2

Test #	Active Agent	Number of Carbons	Product (Isomorph)
1	Propionic acid	3	Aragonite
2	Lactic acid	3	Aragonite
3	Pyruvic acid	3	Aragonite
4	Acrylic acid	3	Aragonite
5	Methoxyacetic acid	3	Aragonite
6	Methacrylic acid	4	Aragonite
7	Butanoic acid	4	Aragonite
8	Pentanoic acid	5	Aragonite
9	Hexanoic acid	6	Aragonite
10	Heptanoic acid	7	Aragonite
11	Octanoic acid	8	Aragonite
12	Phthalic acid	8	Calcite
13	2-Ethylhexanoic acid	8	Aragonite
14	Nonanoic acid	9	Aragonite
15	Azelaic acid	9	Aragonite
16	Trimelitic acid	9	Calcite
17	Decanoic acid	10	Aragonite
18	Undecanoic acid	11	Aragonite
19	4-ButylBenzoic acid	11	Aragonite
20	Dodecanoic acid	12	Aragonite
21	Palmitic acid	16	Aragonite
22	Stearic acid	18	Aragonite
23	Oleic acid	18	Aragonite
24	$MgCl_2$	-	Aragonite
25	$AlCl_3$	-	Aragonite
26	$C_{12}H_{25}C_6H_4SO_3H$ (LABSA)	18	Aragonite

EXAMPLE 3 - A Batch Mode of Operation:

A batch mode of operation, of which parameters were as close as possible to those of EXAMPLE 1, was attempted. Only particulate precipitated calcite of rhombohedral shape was obtained. No particulate precipitated aragonite could be obtained when using decanoic acid or any other active agent that was mentioned as being effective in EXAMPLE 1. The experiment was conducted as follows:

The active agents were investigated by producing precipitated calcium carbonate particles according to the following procedure:

2 kg aqueous calcium hydroxide slurry, containing already the respective active agent (c.f. EXAMPLE I) were added to the 3.2 l stainless steel 316 reactor of EXAMPLE 1. The Dissolver was operated at 4000 rpm, the temperature was maintained at 85°C and the production rate was determined by controlling the feed rate of the carbon dioxide gas. The carbonation was stopped after about 20-30 minutes, when the pH reached 7. The product mixture was then removed from the reactor through its bottom outlet.

The resulting slurry was filtered through a filter cloth on the Buchner using a vacuum pump to dewater the product. The filter cake was dried for 12 hours at 120°C and the crystallographic morphologies and the shapes of the crystals of the precipitated calcite particles were determined using XRD and SEM analyses, respectively. As mentioned above, no precipitated aragonite particles were obtained.

The process set points - batch mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10m/sec.).
2. pH = ~14 → 7.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = 2 kg.
6. Potential active agent concentration = 1 wt.%, based on $CaCO_3$.

EXAMPLE 4 - Parametric Studies - the Effect of the Temperature:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed – 12 m/sec.).
2. pH = 9.5.
3. Temperature = variable.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5 wt.%, based on $CaCO_3$.

Table 3- the results of EXAMPLE 4

Test #	Temperature °C	Mineralogical Phase XRD
1	87	Aragonite
2	80	Aragonite
3	70	Aragonite
4	60	Aragonite
5	50	Calcite

EXAMPLE 5 - Parametric Studies - Effect of the pH:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed – 12 m/sec.).
2. pH = variable.
3. Temperature = 87°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour)

5. Aqueous calcium hydroxide slurry (of Shfeya) ~10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).

5. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 4- the results of EXAMPLE 5

Test #	pH	Mineralogical Phase XRD
1	10	Aragonite
2	9.5	Aragonite
3	9	Aragonite
4	8.5	Aragonite
5	8.0	Calcite
6	7.0	Calcite

EXAMPLE 6 - Parametric Studies - Concentration Effect of the Active Agent

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).

2. pH = 9.5. 3. Temperature = 87°C.

4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).

5. Aqueous calcium hydroxide slurry (of Shfeya) ~10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).

6. Active agent concentration = decanoic acid; variable wt.%; based on $CaCO_3$.

Table 5- the results of EXAMPLE 6

Test #	Decanoic acid % (wt)	Mineralogical Phase XRD
1	1.0	Aragonite
2	0.5	Aragonite
3	0.3	Aragonite + Calcite*
4	0.2	Aragonite + Calcite*
5	0.1	Calcite

* - A crystallographic purity (aragonite/(aragonite + calcite)) <90%.

Note:

Though the present invention is especially aimed at obtaining substantially pure particulate precipitated aragonite calcium carbonate of crystallographic purity (aragonite phase/(aragonite phase + calcite phase)) ?90% and even >95%, there are still applications that can utilize mixtures of these isomorphs where such crystallographic purity is <90%, and such mixtures are within the scope of the present invention. In such cases the boundary conditions of the present invention (c. f. Tests #3 and #4, above) may still be used.

EXAMPLE 7 - Parametric Studies - Concentration Effect of the $Ca(OH)_2$

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12m/sec.).
2. pH = 9.5.
3. Temperature = 87°C .
4. Carbon dioxide flow r= 180 L.P.H. (liters/hour)
5. Aqueous calcium hydroxide slurry (of Shfeya) -variable wt.% = ~ variable L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 6- the results of EXAMPLE 7

Test #	Solids in Slaked Lime % (wt)	Mineralogical Phase XRD
1	8	Aragonite
2	4	Aragonite
3	3	Aragonite + Calcite*
4	2	Aragonite + Calcite*
5	1	Calcite

* - A crystallographic purity (aragonite : (aragonite + calcite)) <90% and c.f. the above note at the end of Example 6.

EXAMPLE 8 - Parametric Studies - Rotor Speed Effect:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = variable rpm (Tip Speed ~ variable).
2. pH = 9.5.
3. Temperature = 87°C.
4. Carbon dioxide flow rate = 180 L.P.H (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 7- the results of EXAMPLE 8

Test #	Rotor Speed rpm	Tip Speed m/sec.	Mineralogical Phase XRD
1	10000	25	Aragonite
2	4800	12	Aragonite
3	2000	5	Aragonite + Calcite*
4	1000	2.5	Calcite

* - A crystallographic purity (aragonite : (aragonite + calcite)) <90% and c.f. the above note at the end of Example 6.

EXAMPLE 9 - Parametric Studies - Effect of the CO_2 Flow Rate (F.R.)

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = 87°C .
4. Carbon dioxide flow rate = variable L.P.H. (liters/hour)
5. Aqueous calcium hydroxide slurry (of Shfeya) -variable wt.% = ~ variable L.P.H. (to maintain the preset pH value).

6. Active agent concentration = decanoic acid; 0.5 wt.% based on $CaCO_3$.

Table 8- the results of EXAMPLE 9

Test #	CO_2 Flow Rate L.P.H.	Mineralogical Phase XRD
1	240	Aragonite
2	180	Aragonite
3	120	Aragonite

EXAMPLE 10 - Parametric Studies - Effect of the CO_2/Air Ratio:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = 87°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10% (wt) = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5 wt.%; based on $CaCO_3$.
7. Air = variable.

Table 9- the results of EXAMPLE 10

Test #	Air/CO_2	Mineralogical Phase XRD
1	0	Aragonite
2	0.33	Aragonite
3	0.66	Aragonite

EXAMPLE 11 - The Effect of Active Agent on Content of the Wet Filter Cake:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only. The content of $CaCO_3$ in the wet filter cake was determined after drying 12 hours at 120°C. Relatively pure (aragonite phase/(aragonite phase + calcite

phase)) ≥95% and dry precipitated acicular aragonite calcium carbonate particles were obtained. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4800 rpm (Tip Speed ~ 12 m/sec.).
2. pH = 9.5.
3. Temperature = 90°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.7; 1.0; 2.0 wt.%; based on $CaCO_3$.

Table 10- the results of EXAMPLE 11

Test #	Dosage % (wt)	Product (Isomorph)	$CaCO_3$ % (wt)*	Crystallographic Purity**
1	0.7	Aragonite	>80	≥95%
2	1.0	Aragonite	>80	≥95%
3	2.0	Aragonite	>80	≥95%

* - % (wt) $CaCO_3$ = 100 x wt. of dry filter cake / wt. of wet filter cake

** - As determined by the XRD analyses (for Test #2 - c.f. Figs. 4 and 5)

Note:

By choosing relatively standard conditions for the present process, it is possible to reduce the water content in the wet filter cake below 20 wt.%.

EXAMPLE 12 - The Effect of the Active agent on the Resistivity to Acids:

Similar experiments to EXAMPLE 1 were conducted using decanoic acid only, the resistivity of the dry samples to acidic aqueous solutions being determined as follows. A 5 l solution of HCl in water at pH=3.5 was prepared for all the following experiments, so as to assure equal starting experimental conditions. 100 ml of this HCl solution were poured into a 100 ml graduated cylinder, 5 g of precipitated $CaCO_3$ particles were added and the pH was measured after 20

minutes. Evolution of CO_2 was observed visually, as was the behavior of the commercial sample #C, the calcite #BM-37, and it was found that the aragonite samples of the present invention (#12-3, #12-4, #12-5) were markedly different. It is worthwhile to note that sample #12-5 produced few bubbles that did not detach from the surface of the precipitated aragonite particles. The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 5200 rpm.(Tip Speed – 13 m/sec.).
2. pH = 9.5. 3. Temperature = 90°C.
3. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
4. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
5. Active agent concentration = decanoic acid; 0.7%; 1.0 %; 2% wt.% based on $CaCO_3$.

Table 11- the results of EXAMPLE 12

Test #	Sample #	Active agent (wt.%)	Product (Isomorph)	pH after 20 mins.	Note
1	C*	Unknown	Aragonite	>6	Violent Evolution of CO_2
2	BM-37**	1.0	Calcite	>5	Evolution of CO_2
3	12-3	0.7	Aragonite	<4	Slight Evolution of CO_2
4	12-4	1.0	Aragonite	<4	Slight Evolution of CO_2
5	12-5	2.0	Aragonite	<4	No Evolution of CO_2

* - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40

** - This sample was taken from the batch mode of operation in EXAMPLE 3

Note:

By choosing relatively standard conditions for the present process, it is possible to increase the resistance of the product towards acids by using quite low concentrations of the active agent and obtain excellent product for the paper industry of which processes are acidic and for the coating industry for durable paints for acidic environments.

EXAMPLE 13 - Effect of Raw Material/Process on Whiteness of the Product:

EXAMPLE 1 and EXAMPLE 3 were conducted using the aqueous calcium hydroxide slurries of PREPARATION I and of PREPARATION II for comparison. The whitenesses of the products are compared.

The results are as follows:

The process set points - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.).
2. pH = 9.5.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour)
5. Aqueous calcium hydroxide slurry (of Arad/Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 1 wt.% based on $CaCO_3$.

The process set points - batch mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed ~ 10 m/sec.).
2. pH = ~14 → 7.
3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Arad/Shfeya) - 10 wt.% = 2 kg.
6. Active agent concentration = decanoic acid 1 wt.% based on $CaCO_3$.

Table 12- the results of EXAMPLE 13

CaO of Arad (whiteness = >95%)		CaO of Shfeya (whiteness = ~88%)	
Continuous	Batch	Continuous	Batch
AR-83A	BM37A	AR-83	BM37
Aragonite $CaCO_3$	Calcite $CaCO_3$	Aragonite $CaCO_3$	Calcite $CaCO_3$
Whiteness=98-9%	Whiteness=97-8%	Whiteness=97-9%	Whiteness=92-5%

Notes:

1. When the raw material (CaO) is relatively pure, the whiteness of the products (AR-83A and BM37A) is not (and should not be) much different. However, when the CaO is relatively impure, the whiteness of the precipitated aragonite particles (AR-83) is dramatically higher than the corresponding calcite (BM37), due to the unique effect of the process of the present invention.

2. The whiteness of the precipitated particulate aragonite obtained according to the present process attains top quality, independently of the CaO source.

EXAMPLE 14 - Effect of the Active Agent/Process on the Specific Gravity (S.G.) of precipitated particulate calcium carbonate:

EXAMPLE 1 was repeated using the aqueous calcium hydroxide slurry of PREPARATION I, except that the concentration of decanoic acid was gradually increased.

(A) Determination of the Specific Gravity (S.G.) of a Product Dried at 120°C

1. The wet filter cake of the $CaCO_3$ sample was dried for 12 hours at 120°C to remove all free water.

2. A weighed quantity of the dry $CaCO_3$ sample (Wc) + a weighed quantity of tall oil (Wo) (Density of 0.93 g/cm^3) were introduced into a 1 l glass beaker.

3. The mixture was stirred with the Hasiangtai HD-550 Dissolver for 10 minutes, at 4000 rpm (using a saw-blade rotor of d = 4.8 cm).

4. The slurry was poured into a 250 ml graduated glass settling column and was sonicated in an ultrasound bath for 20 minutes, until all the trapped bubbles were released.

5. The settling column was then evaluated at 20-22°C for:

(a) the volume of the slurry - V

(b) the total net weight of the slurry - W

Based on the above measurements, the following was calculated:

(1) from the equation: D = W/V g/cm^3, the density of the slurry;

(2) from the equation

1/D = [Wc(Wo + Wc)]/S.G. + [Wo(Wo+Wc)]/0.93,

the S.G. of the $CaCO_3$ sample was calculated.

6. The loose bulk density (B.D.) of the dry powder was measured using a balance and a graduated cylinder.

The process set points - continuous mode of operation:

1. Rotor Speed = 4000 rpm (Tip Speed – 10 m/sec.)
2. pH = 9.5. 3. Temperature = 85°C.
4. Carbon dioxide flow rate = 180 L.P.H. (liters/hour).
5. Aqueous calcium hydroxide slurry (of Shfeya) -10 wt.% = ~ 6 L.P.H. (to maintain the preset pH value).
6. Active agent concentration = decanoic acid; 0.5; 1; 2; 5; 2; 1 wt.% based on $CaCO_3$.

The results are as follows

Table 13- the results of EXAMPLE 14 (A)

Test #	Sample Code	Active agent	Dosage (wt.%)	Mineralogical Phase XRD	S.G.† g/cm³	Loose B.D.† g/cm³
1	Natural $CaCO_3$	-	-	Calcite	2.63	0.65
2	BM-37*	decanoic acid	1	Calcite	2.54	0.37
3	C**	N.A.	N.A.	Aragonite	2.56	0.54
4	AR-81	decanoic acid	0.5	Aragonite	2.02	0.31
5	AR-83	decanoic acid	1	Aragonite	1.90	0.30
6	AR-118	decanoic acid	2	Aragonite	1.75	0.25
7	AR-119	decanoic acid	5***	Aragonite	1.67	0.29
8	AR-135	nonanoic acid	1	Aragonite	1.88	0.31
9	AR-120	decanoic acid	2^	Aragonite	1.72	0.23

* - The sample was taken from the batch mode of operation in - EXAMPLE 3.
** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.
*** - 5g of AR-119 were dissolved in a 10% HCl solution. The decanoic acid was extracted with 1,2-dichloroethane. HPLC analysis using a C18 column revealed 4.93% (wt; based on the calcium carbonate) of this acid in the sample.
^ - 50ppm of phosphoric acid were used in addition to the decanoic acid to increase the aspect ratio of the acicular aragonite.
† - A dry powder after drying for 12 hours at 120°C. N.A. - Not available.

Notes:

1. The determination of a specific gravity (S.G.) of particulate precipitated aragonite calcium carbonate of the present invention, in a range below 2.5 g/cm³ (after drying at 120°C for twelve hours as described above, as well as after ignition of the dried material at 500°C for eight hours) is actually a most important and most decisive test to consider if the technology that was used is under the domain of the present invention.
2. Only the inclusion of gas (probably, as tiny bubbles or "blisters") in closed pores can account for the dramatic reduction of the S.G. of particulate precipitated

aragonite calcium carbonate of the present invention. The L.O.D. and the L.O.I. in the latter tests (c. f. (B) and (C), respectively) do not leave many logical choices to account for this phenomenon. Also, this is in accordance with the facts i. that the product of the present invention is obtained under flotation conditions, and ii. that the high hiding power of the paints, in which the particulate precipitated aragonite calcium carbonate of the present invention was used, are probably due to the high effective refractive index of this product of the present invention, which is much higher than that expected of similar products that are produced according to the prior art (c. f. data collected in EXAMPLE 15 and the comparison made to paint formulations that were based on raw materials of the prior art).

3. The idea of using porous particles, to increase their effective refractive index in coatings, is not new. For instance, Rohm & Haas produces a series of such products, e. g. Ropaque® OP96 and Ropaque® OP3000. However, these particles are of an organic polymeric nature of which cost and adaptation to the environment is not to be compared with precipitated calcium carbonate particles.

(B) Determination of the Specific Gravity (S.G.) of a Product Calcined at 300°C

1. The wet filter cake of the $CaCO_3$ sample was dried for 12 hours at 120°C to remove all the free water.

2. The weighed dry sample was heated for 8 hours at 300°C. The loss on drying (L.O.D.) was then determined.

3. The S.G. of the heated powder was measured as above (c. f. (A)).

4. The loose bulk density (B.D.) of the dry powder was measured using a balance and a graduated cylinder.

The results are as follows:

328

Table 14- the results of EXAMPLE 14 (B)

Test #	Sample Code	Active agent	Dosage (wt.%)	L.O.D. wt.% 300°C	S.G.† g/cm³	Loose B.D.† g/cm³
10	Natural $CaCO_3$	-	-	0.10	2.63	0.651
11	BM-37*	decanoic acid	1	2.21	2.64	0.372
12	C**	N.A.	N.A.	1.3	2.63	0.54
13	AR-81	decanoic acid	0.5	0.83	2.19	0.255
14	AR-83	decanoic acid	1	0.89	2.11	0.285
15	AR-118	decanoic acid	2	2.32	2.03	0.200
16	AR-119	decanoic acid	5	5.73	2.01	0.200
17	AR-135	nonanoic acid	1	0.95	2.12	0.238
18	AR-120	decanoic acid	2^	2.27	2.02	0.235

* - The sample was taken from the batch mode of operation in-EXAMPLE 3.
** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.
^ - 50ppm of phosphoric acid were used in addition to the decanoic acid.
† - A dry powder after heating for 8 hours at 300°C.
N.A. - Not available.

(C) Determination of the Specific Gravity (S.G.) of a Product Calcined at 500°C

1. The wet filter cake of the $CaCO_3$ sample was dried for 12 hours at 120°C to remove all the free water.

2. The dry sample was calcined for 8 hours at 500°C. The loss on ignition (L.O.I.) was then determined.

3. The S.G. of the calcined powder was measured as above.

4. The loose bulk density (B.D.) of the dry powder was measured using a balance and a graduated cylinder.

The results are as follows:

Table 15- the results of EXAMPLE 14 (C)

Test #	Sample Code	Dosage %(wt)	L.O.I. %(wt) 500°C^^	S.G.† g/cm³	Loose B.D.† g/cm³
19	Natural $CaCO_3$	-	0.18	2.70	0.75
20	BM-37	1*	2.58	2.60	0.38
21	C**	N.A.	2.02	2.71	0.55
22	AR-81	0.5	1.32	2.13	0.23
23	AR-83	1	1.44	2.03	0.22
24	AR-118	2	2.07	2.01	0.18
25	AR-119	5***	5.25	1.83	0.19
26	AR-135	1	1.44	2.01	0.24
27	AR-120	2^	2.37	1.91	0.18

* - The sample was taken from the batch mode of operation in-EXAMPLE 3.
** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.
*** - 5g of AR-119 were dissolved in a 10% HCl solution. No decanoic acid could be extracted or detected, as is expected of such molecules when they are subjected to heating for 8 hours at 500°C.
^ - 50ppm of phosphoric acid were used in addition to the decanoic acid.
^^ - Aragonite is converted into calcite at T > 400°C.
† - A dry powder after drying for 12 hours at 120°C and thereafter heating for 8 hours at 500°C.
N.A. - Not available.

EXAMPLE 15 - Preparation of Exterior White Paint - Hercules Inc.

The procedure for the preparation of this paint was obtained from Hercules Inc.; Cellulose & Protein Products D.; Wilmington, DE 19899 (USA). The procedure followed quite closely the Celanese Resins Formulation No. EP-48-222 for the production of this Exterior White Paint (Vinyl Acetate & Acrylate).

(A) The ingredients used for the 52% PVC Paint and their function are as follows:

1. Tap water.
2. Nopco NDW defoamer.
3. Cellosize QP 15000 thickener (hydroxy ethyl cellulose).
4. Disperse One (45% N.V.) (dispersant).
5. Synperonic NP10 surfactant; wetting agent.
6. Kronos 2160 TiO_2 pigment.
7. Synthetic sodium aluminum silicate (p820) (spacer)
8. Kaolin clay (D_{50} = 3.1 micron)(spacer)
9. $CaCO_3$ (spacer) - A GCC product of Polichrom Ltd., Israel
10. Talc (D_{50}=12.3 micron)(spacer)
11. PCC - Aragonite of the present invention (samples used contained >80% $CaCO_3$ in the wet cake products before their drying; no diminution operation took place prior to this use. Namely, the PCC - Aragonite used is not necessarily yet optimized for its purpose).
12. Copolymer vinyl acetate acrylate (55% N.V.) (emulsion)
13. Butyl diglycol acetate solvent (coalescent agent)
14. Kathon LXE preservative.
15. 25% Ammonia (base).
16. Tap water.

Tap water (1), defoamer (2) and thickener (3) were added to a plastic container (d=20 cm; h=30 cm) equipped with a disk (d=8 cm) attached to a Dissolver (Homo Dispers Model HD-550 (0.75 HP) of Hsiangtai Machinery Industry Co. Ltd.; Taiwan). The mixture was stirred at 500 rpm for 5 minutes, after which the dispersant (4) and the wetting agent (5) were added, and stirring was continued at

500 rpm for additional 5 minutes. At this point the stirring speed was increased to 1500 rpm and the respective ingredients for the respective formulations 1- 10 were added consecutively, each ingredient over a 5 minute period, according to the order in the above list of reagents (6 - 16).

The physical properties of the above paints were measured, including the most important property - the hiding power (%) of 90 µm layers of paint were determined with an ACS instrument (Applied Color Systems) and the results are given in the following Tables 16 and 17:

Table 16 - the results of EXAMPLE 15

Exterior White Paint - Hercules Inc. Evaluation of the 52% PVC Paints Based on the Precipitated Aragonite Calcium Carbonate Particles of the Present Invention (PCC - Aragonite)						
	1	2	3	4	5	6
Raw Material	% (wt)					
Tap Water	25.0	25.0	25.0	25.0	25.0	25.0
Defoamer	0.1	0.1	0.1	0.1	0.1	0.1
Thickener(15K)	0.3	0.3	0.3	0.3	0.3	0.3
Dispersant (45%)	0.9	0.9	0.9	0.9	0.9	0.9
Wetting Agent	0.35	0.35	0.35	0.35	0.35	0.35
TiO_2; Kronos	14.0	9.0	9.0	9.0	9.0	8.4
Silicate	3.7	3.7	3.7	3.7	4.0	3.9
$CaCO_3$ - GCC	7.0	-	-	-	-	-
Kaolin Clay	6.5	6.5	6.5	6.5	10.7	6.8
Talc	6.9	-	-	-	-	-
PCC-Aragonite*	-	17.75	17.75	17.75	13.00	17.75
Copolymer (55%)	24.5	25.5	25.5	25.5	25.4	25.4
Coalescent Agent	0.1	0.1	0.1	0.1	0.1	0.1
Preservative	0.5	0.5	0.5	0.5	0.5	0.5
Ammonia	0.3	0.3	0.3	0.3	0.3	0.3
Tap Water	10.45	10.0	10.0	10.0	10.35	10.2
Total	100.	100.	100.	100.	100.	100.
The Characteristics of the Paint						
Solids (%)	50.98	50.98	50.98	50.98	50.67	50.82
P.V.C. (%)	51.77	51.32	51.32	51.32	51.51	51.55
Hiding Power (%)	94.0	94.4	94.9	95.5	95.1	94.9
Viscosity (K.U.)	92.0	92.0	93.2	98.0	100.0	98.0
Hegman	4.5	5.5	5.5	5.0	4.0	4.5
Bulk Density (g/cm^3)	1.317	1.259	1.257	1.248	1.228	1.221
Saving of TiO_2 (%)	-	35.7	36.7	35.7	35.7	40.0
Weight Saving (%)	-	4.4	4.6	5.2	6.9	7.3

Formulation No.	Pigment*	Sample Code	Active Agent	Active Agent % (wt)
1	Reference Paint	-	-	-
2	PCC - Aragonite	AR-81	Decanoic acid	0.5
3	PCC - Aragonite	AR-83	Decanoic acid	1.0
4	PCC - Aragonite	AR-118	Decanoic acid	2.0
5	PCC - Aragonite	AR-119	Decanoic acid	5.0
6	PCC - Aragonite	AR-119	Decanoic acid	2.0

Table 17 - the results of EXAMPLE 15

Exterior White Paint - Hercules Inc. Evaluation of the 52% PVC Paints Based on the Precipitated Aragonite Calcium Carbonate Particles of the Present Invention (PCC - Aragonite)						
	1	7	8	9	10	
Raw Material	% (wt)					
Tap Water	25.0	25.0	25.0	25.0	25.0	
Defoamer	0.1	0.1	0.1	0.1	0.1	
Thickener(15K)	0.3	0.3	0.3	0.3	0.3	
Dispersant (45%)	0.9	0.9	0.9	0.9	0.9	
Wetting Agent	0.35	0.35	0.35	0.35	0.35	
TiO_2; Kronos	14.0	7.0	7.0	6.3	12.0	
Silicate	3.7	4.8	4.2	4.2	3.7	
$CaCO_3$ - GCC	7.0	-	-	-	-	
Kaolin Clay	6.5	7.1	12.6	13.1	6.5	
Talc	6.3	-	-	-	-	
PCC-Aragonite**	-	17.75	13.0	13.0	15.3*	
Copolymer (55%)	24.5	25.5	26.0	26.0	24.5	
Coalescent Agent	0.1	0.1	0.1	0.1	0.1	
Preservative	0.5	0.5	0.5	0.5	0.6	
Ammonia	0.3	0.3	0.3	0.3	0.3	
Tap Water	10.45	10.3	9.75	9.85	10.45	
Total	100.	100.	100.	100.	100.	
The Characteristics of the Paint						
Solids (%)	50.98	50.98	50.98	50.98	50.98	
P.V.C. (%)	51.77	51.32	51.32	51.32	51.91	
Hiding Power (%)	94.0	94.2	94.3	94.0	92.7	
Viscosity (K.U.)	92.0	96.8	96.8	96.0	90.2	
Hegman	4.5	4.5	4.5	4.5	4.5	
Bulk Density (g/cm³)	1.317	1.179	. 1.159	1.224	1.300	
Saving of TiO_2 (%)	-	50.0	50.0	55.0	14.3	
Weight Saving (%)	-	10.5	12.0	7.0	1.3	

Formulation No.	Pigment*	Sample Code	Active Agent	Active Agent % (wt)
1	Reference Paint	-	-	-
7	PCC - Aragonite	AR-118	Decanoic acid	2.0
8	PCC - Aragonite	AR-119	Decanoic acid	5.0
9	PCC - Aragonite	AR-119	Decanoic acid	5.0
10	PCC - Aragonite	C**	N.A.	N.A.

** - Commercial PCC - Aragonite; of Specialty Minerals Inc. (SMI); Opacarb® A40.

(B) <u>The ingredients of the 32% PVC Paint and their function are as follows:</u>

1. Tap water. 2. Nopco NDW defoamer.
3. Cellosize QP 15000 thickener (hydroxy ethyl cellulose).
4. Disperse One (45% N.V.) (dispersant).
5. Synperonic NP10 surfactant; wetting agent.
6. Kronos 2160 TiO_2 pigment. 7. Synthetic Na-Al silicate (p820) (spacer).
8. Kaolin clay (D_{50} = 3.1 micron)(spacer)
9. $CaCO_3$ (spacer) - a GCC product of Polichrom Ltd., Israel
10. Talc (D_{50}=12.3 micron)(spacer)
11. PCC - aragonite of the present invention (samples used contained >80% $CaCO_3$ in the wet cake products before their drying; no diminution operation took place prior to this use. However, the PCC - aragonite used is not necessarily yet optimized for its purpose).
12. Propylene glycol (solvent).
13. Copolymer vinyl acetate acrylate (55% N.V.) (emulsion).
14. Butyl diglycol acetate solvent (coalescent agent).
15. Kathon LXE preservative. 16. 25% Ammonia (base). 17. Tap water.

Tap water (1), defoamer (2) and thickener (3) were added to a plastic container (d=20 cm; h=30 cm) equipped with a disk (d=6 cm) attached to a Dissolver (Homo Dispers Model HD-550 (0.75 HP) of Haiangtai Machinery Industry Co. Ltd.; Taiwan). The mixture was stirred at 500 rpm for 5 minutes, after which the dispersant (4) and the wetting agent (5) were added, and stirring was continued at 500 rpm for additional 5 minutes. At this point the stirring speed was increased to 1500 rpm and the respective ingredients for the respective formulations 1- 10 were added consecutively, each ingredient over a 5 minute period, according to the order in the above list of reagents (6 - 15).

The physical properties of the above paints were measured, including the most important property - the hiding power (%) of 90 μm layers of paint were determined with an ACS Instrument (Applied Color Systems) and the results are given in the following Table 18:

Table 18 - the results of EXAMPLE 15

Exterior White Paint - Hercules Inc. Evaluation of the 32% PVC Paints Based on the Precipitated Aragonite Calcium Carbonate Particles of the Present Invention (PCC - Aragonite)						
	11	12	13	14	15	16
Raw Material	% (wt)					
Tap Water	17.8	17.8	17.8	17.8	17.8	17.8
Defoamer	0.15	0.15	0.15	0.16	0.15	0.15
Thickener(15K)	0.22	0.22	0.22	0.22	0.22	0.22
Dispersant (45%)	0.60	0.60	0.60	0.60	0.60	0.60
Wetting Agent	0.34	0.34	0.34	0.34	0.34	0.34
TiO2; Kronos	22.5	20.0	20.0	19.0	18.0	19.0
Silicate	2.25	2.25	2.25	2.25	2.25	-
CaCO3 - GCC	5.0	-	-	-	-	-
PCC-Aragonite*	-	7.5	7.5	8.5	9.25	13.0
Propylene Glycol	2.70	2.70	2.70	2.70	2.70	2.70
Copolymer (55%)	37.45	37.45	37.45	37.45	36.0	33.4
Coalescent Agent	0.18	0.18	0.18	0.18	0.18	0.18
Preservative	0.45	0.45	0.45	0.45	0.45	0.45
Ammonia	0.30	0.30	0.30	0.30	0.30	0.30
Tap Water	10.06	10.06	10.06	10.06	9.76	11.86
Total	100.	100.	100.	100.	100.	100.
The Characteristics of the Paint						
Solids (%)	50.35	50.35	50.35	50.35	50.35	50.37
P.V.C. (%)	32.59	32.64	32.64	32.93	32.64	38.73
Hiding Power (%)	91.0	91.4	91.4	91.0	90.8	91.0
Viscosity (K.U.)	87.2	98.0	97.4	96.2	87.8	90.2
Hegman	5.5	5.5	5.5	5.5	5.0	5.5
Bulk Density (g/cm³)	1.18	1.128	1.127	1.109	1.005	1.073
Saving of TiO_2 (%)	-	11.1	11.1	15.5	20.0	15.5
Weight Saving (%)	-	4.4	4.5	6.0	14.8	6.8

Formulation No.	Pigment*	Sample Code	Active Agent	Active Agent % (wt)
11	Reference Paint	-	-	-
12	PCC - Aragonite	AR-118	Decanoic acid	2.0
13	PCC - Aragonite	AR-119	Decanoic acid	5.0
14	PCC - Aragonite	AR-119	Decanoic acid	5.0
15	PCC - Aragonite	AR-119	Decanoic acid	5.0
16	PCC - Aragonite	AR-118	Decanoic acid	2.0

Notes:

1. The particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite) can be used to produce paints without a substantial prior size reduction, except that effected by the mixing system of the production of the paint, which is anyway being used in this art to thoroughly disperse the pigments in the various formulations.

2. Though the particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite) is not yet optimized for its use in the production of paints and though the formulations used are by no means optimized, still this product is able to substitute over 50% of the expensive titanium oxide pigment without any deterioration of the resulting paint, as it manifested by the hiding power measured.

3. As the coatings (paints) are being sold and used by volume, and not by weight, the additional saving resulting from using the particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite) can surpass 10% on all the constituents of the coating, including the titanium oxide.

4. For simplicity in formulating the above mentioned paints, dry samples of The particulate precipitated aragonite calcium carbonate of the present invention (PCC-Aragonite), were used. However, wet filter cakes that contain even more water than 20% wt.%, based on wet $CaCO_3$ cake, can be used, provided that this water is being taken in account. However, on an industrial scale, dry PCC-Aragonite will be rarely used, due to the economy of using the wet product.

While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.

CLAIMS

1. A process for producing a particulate precipitated aragonite calcium carbonate, which comprises reacting an aqueous calcium hydroxide slurry with a gas selected from the group consisting of carbon dioxide and a gas containing it, wherein the parameters of said process, including at least one preselected active agent, mode of operation, operating concentrations of raw materials, operating temperature, operating mixer speed and operating pH, are such that (A) the specific gravity of the product after drying for 12 hours at 120°C is <2.5 g/cm^3;and (B) the specific gravity of this dry product after ignition for eight hours at 500°C is <2.5 g/cm^3.

2. A process according to claim 1, which is further characterized by the following features:

(a) said at least one active agent is selected from the group consisting of carboxylic acids of formula $CH_3(CH_2)_nCOOH$, where n is 7-9, their carboxylate salts, their acid anhydrides, their esters, their acyl halides and ketenes of the formula $CH_3(CH_2)_{n-1}C=C=O$, where n is 7-9;

(b) said concentration of the at least one active agent is within the range between 0.2 wt.% and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate;

(c) said slurry contains calcium hydroxide in a concentration within the range of from 3 to 30 wt.%;

(d) said pH is within the range of from 8 to 11;

(e) said temperature is in the range between 60°C and the boiling temperature of the reaction mixture;

(f) said mode of operation is selected from a continuous and a semi-continuous (intermittent) mode of operation;

(g) said mixer peripheral speed (tip-speed) is above 5 m/sec;

(h) said at least one active agent is added in a manner selected from introduction into the carbonation reactor and premixing with said calcium hydroxide slurry prior to reaction with said gas.

3. A process according to claim 2, which is further characterized by at least one of the following features:

(a) said at least one active agent is selected from the group consisting of carboxylic acids of formula $CH_3(CH_2)_nCOOH$, where n is 7-9, and the calcium salts thereof;

(b) said concentration of the at least one active agent is within the range between 0.3 wt.% and 5 wt.%, calculated as the $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate;

(c) said slurry contains calcium hydroxide in a concentration within the range of from 4 to 20 wt.%;

(d) said pH is within the range of from 9 to 10;

(e) said temperature is in the range between 80°C and the boiling temperature of the reaction mixture;

(f) said mode of operation is a continuous mode of operation.

4. A process according to claim 3, which is further characterized by at least one of the following features, namely:

said active agent is selected from the group consisting of decanoic acid and the calcium salts thereof,

said concentration of said at least one active agent is within the range between 0.4 wt.% and 3 wt.%, calculated as the $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate,

said temperature is in the range between 90°C and the boiling temperature of the reaction mixture, and

said slurry contains calcium hydroxide in a concentration within the range of from 5 to 15 wt.%.

5. A process according to claim 1, which is conducted as a flotation process in a flotation cell.

6. A process according to claim 5, and substantially as hereinbefore described with reference to Figure 3 of the attached drawings.

7. A particulate precipitated aragonite produced by the process of claim 1, which is characterized by at least one of the following features:
(i) It contains at least one calcium salt of carboxylic acids selected from those of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7, 8, and 9, in an amount between 0.2 and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate;
(ii) it has an XRD spectrum substantially in accordance with Figure 5 of the attached drawings.

8. A particulate precipitated aragonite according to claim 7, having a specific gravity <2.3 g/cm^3 after drying at 120°C for twelve hours, and a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500°C.

9. A particulate precipitated aragonite according to claim 7, having a specific gravity <2.0 g/cm^3 after drying at 120°C for twelve hours.

10. A particulate precipitated aragonite according to claim 7, having a specific gravity <1.8 g/cm^3, after drying at 120°C for twelve hours.

11. A particulate precipitated aragonite according to any of claims 7 to 10, of crystallographic purity (aragonite/(aragonite + calcite)) at least 90%.

12. A particulate precipitated aragonite according to any of claims 7 to 10, of crystallographic purity (aragonite/(aragonite + calcite)) <90%.

13. A particulate precipitated aragonite which has (A) a specific gravity <2.5 g/cm^3 after drying for 12 hours at 120°C, and (B) a specific gravity <2.5 g/cm^3 after ignition for eight hours at 500°C of the product dried in (A).

14. A particulate precipitated aragonite according to claim 13, which is further characterized by at least one of the following features:

(i) it contains at least one calcium salt of carboxylic acids selected from those of the general formula: $CH_3(CH_2)_nCOOH$, where n = 7, 8, and 9, in an amount between 0.2 and 10 wt.%, calculated as $CH_3(CH_2)_nCOOH$ and based on the weight of calcium carbonate;

(ii) it has an XRD spectrum substantially in accordance with Figure 5 of the attached drawings.

15. A particulate precipitated aragonite according to claim 13 or claim 14, having (A) a specific gravity <2.3 g/cm^3 after drying at 120 ^oC, and (B) a specific gravity <2.3 g/cm^3 after ignition for eight hours at 500^oC of the product dried in (A).

16. A particulate precipitated aragonite according to claim 13 or claim 14, having a specific gravity <2.0 g/cm^3 after drying at 120^oC for twelve hours.

17. A particulate precipitated aragonite according to claim 13 or claim 14, having a specific gravity <1.8 g/cm^3, after drying at 120^oC for twelve hours.

18 A particulate precipitated aragonite according to claim 13 or claim 14, of crystallographic purity (aragonite/(aragonite + calcite)) at least 90%.

19. A particulate precipitated aragonite according to claim 13 or claim 14, of crystallographic purity (aragonite/(aragonite + calcite)) <90%

ABSTRACT

Disclosed is a novel form of particulate precipitated aragonite calcium carbonate and a novel process for producing it.

SHEET ONE OF FIVE SHEETS

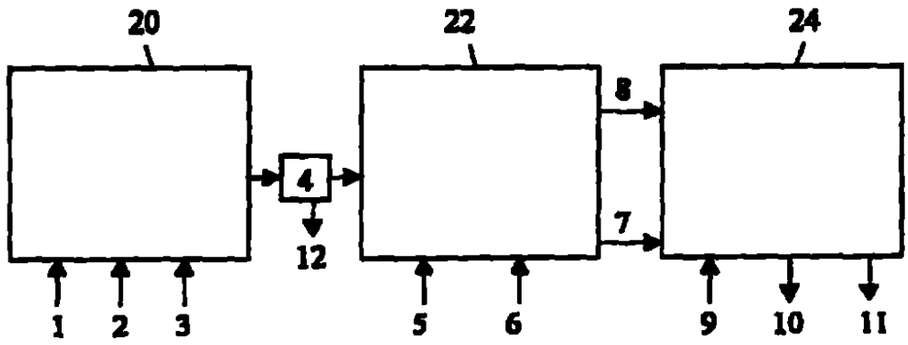

FIGURE 1

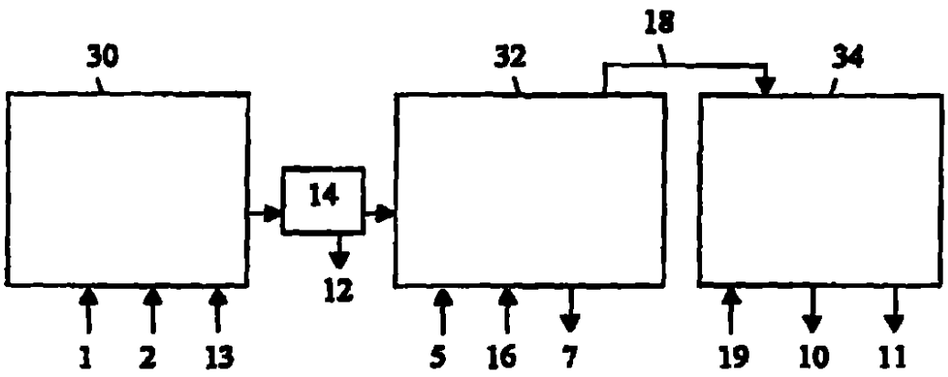

FIGURE 2

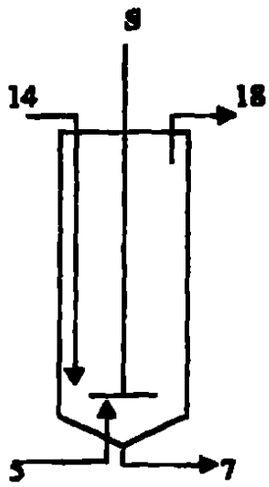

FIGURE 3

SHEET FOUR OF FIVE SHEETS

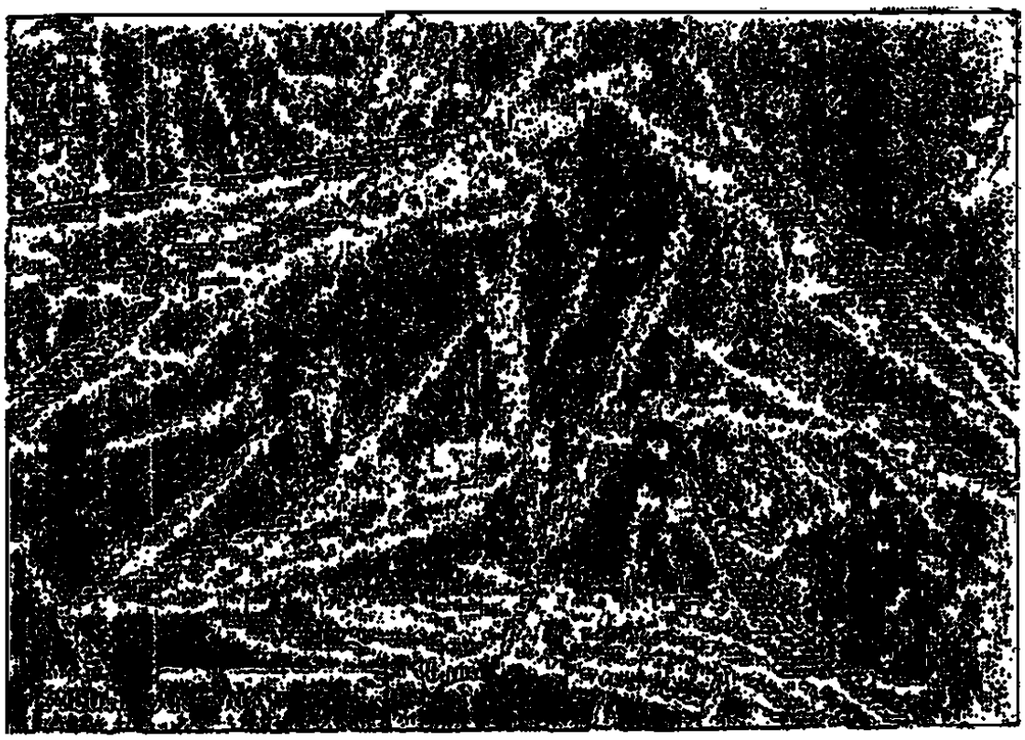

FIGURE 4

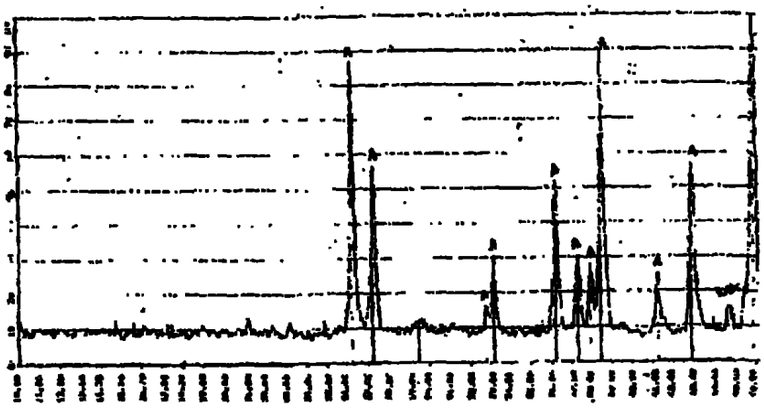

FIGURE 5

Industria y Comercio
SUPERINTENDENCIA

2do. EXAMEN DE FORMA PATENTE DE INVENCION

Folio 372

Radicación no 04-19435

Concepto Técnico no 933 Clasificación Internacional de Patentes C01F 11/18

Practicado el examen de acuerdo a lo establecido en el Art. 38 de la Decisión 486 se determinó que esta solicitud de Patente de Invención:

SI [X] NO [ ] Contiene un resumen de la invención (Art.26-e).

SI [X] NO [ ] Contiene el título o nombre de la invención (Art.27-d).

SI [X] NO [ ] Contiene la descripción de la invención (Art.26-b).

SI [X] NO [ ] NO ES APLICABLE [ ] Contiene los dibujos necesarios para comprender la invención (Art.26-d)

SI [X] NO [ ] Contiene una o más reivindicaciones. (Art.26-c).

SI [ ] NO [ ] NO ES APLICABLE [X] Han sido desarrollados los productos y/o procedimientos a partir de recursos genéticos o de sus productos derivados de los que cualquiera de los Países Miembros es país de origen. (Art. 26- h).

SI [ ] NO [ ] NO ES APLICABLE [X] Los productos y/o procedimientos han sido obtenidos o desarrollados a partir de los conocimientos tradicionales de las comunidades indígenas, afroamericanas, o locales de los países miembros, de acuerdo a lo establecido en la Decisión 391 y sus modificaciones y reglamentaciones vigentes.(Art.26-i).

SI [ ] NO [ ] La invención se refiere a un producto relativo a un material biológico. (Art.26-J).

SI [X] NO [ ] La prioridad coincide con la materia reivindicada.

SI [X] NO [ ] CUMPLE LOS REQUISITOS TÉCNICOS

OBSERVACIONES Y OTROS: SI [X] NO [ ] ver hoja(s) anexa(s)

- NO SE TENDRA EN CUENTA LA FECHA DE PRIORIDAD PORQUE SE PRESENTÓ FUERA DEL PLAZO MENCIONADO EN EL FOLIO 146.
- SE ACEPTA LUEGO RESPONDE FOLIOS 158 A 163.
- SE ACEPTA LUEGO REIVINDICATORIO FOLIOS 130 A 135
- SE ACEPTAN FOLIOS 164 A 169 QUE REEMPLAZAN LOS FOLIOS 20, 42, 63, 68, 69 92 DE LA DESCRIPCIÓN INICIAL.

EXAMINADOR TÉCNICO
JOJOJO

Bogotá D. C., 11 ABRIL 02

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador: 382 0840
Fax: 382 2695
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia

347

Industria y Comercio
SUPERINTENDENCIA

Folio ~~375~~

2020
Bogotá DC

Doctor
MAURICIO JARAMILLO CAMPUZANO
Apoderado

REFERENCIA:	Radicación No.	01-17435
	Trámite	002
	Evento	001
	Actuación	416
	Oficio No.	1126
	Folios	001

Teniendo en cuenta que la solicitud de privilegio de patente que se tramita bajo el expediente indicado en la referencia, reúne los requisitos de forma establecidos en los artículos 26 y 27 de la Decisión 486 de la Comisión de la Comunidad Andina, y en las demás disposiciones vigentes sobre la materia, se envía el extracto de la solicitud a la Oficina de Comunicaciones para efecto de su publicación en la Gaceta de Propiedad Industrial, conforme lo establece el artículo 40 de la misma Decisión.

No obstante lo anterior, no se tendrá en cuenta la prioridad reivindicada No. 09/519,749 del 6 de marzo de 2000, ya que no presentó la documentación dentro del plazo aclarado en el folio 146.

Cúmplase

Dado en Bogotá DC, a los 2002

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

Bogotá, DC,: El extracto de esta solicitud fue publicado en el número de la Gaceta de Propiedad Industrial, de fecha El término hábil señalado por la ley expiró el y SI ___ NO ___ se presentaron oposiciones por parte de terceros.

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador: 382 0840
Fax: 382 2695
E-mail: info@sic.gov.co
Bogotá, D.C., Colombia

202042