SUPERINTENDENCI[illegible]MERCIO

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
INVENTARIO

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División de Nuevas Creaciones

PCT

SOLICITUD

PATENTE DE INVENCION

ENTRADA EN FASE NACIONAL

21. **EXPEDIENTE No.** 08-55574

54 **TITULO** COMPOSICIÓN DE HIPOCLORITO DE CALCIO RECUBIERTA

51. **CLASIFICACION INTERNACIONAL**

71. **SOLICITANTE** ARCH CHEMICALS, INC.

DOMICILIO NORWALK, CT, ESTADOS UNIDOS DE AMÉRICA

74. **APODERADO** JUAN PABLO CADENA SARMIENTO

22. **SANTAFE DE BOGOTA, D.C.**

PETITORIO

AS: 107.411

Industria y Comercio
SUPERINTENDENCIA

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Trs: 11 PATENTEIYII Eve: 378 FASENACIONAL
Act: 411 PRESENTACION Folios: 122

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1 Julio 2008

1 SOLICITUD DE:

☒ Patente de Invención. ☐ Patente de Modelo de Utilidad.

☒ Capítulo I. ☐ Capítulo II.

2 SOLICITANTE (71)	Nombre: **ARCH CHEMICALS, INC.** Dirección: 501 Merritt 7, P.O. Box 5204, Norwalk, CT 06508-5204, Estados Unidos de América Nacionalidad o Domicilio: Estados Unidos de América Lugar de Constitución: Estados Unidos de América Teléfono: Fax: E-mail	**IDENTIFICACIÓN** C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Cual_____ Número _____
3 REPRESENTANTE O APODERADO	Nombre: JUAN PABLO CADENA SARMIENTO Dirección: Cra. 7 No. 71-21 Torre B – Piso 4, Bogotá, Colombia. Teléfono: 744-2200 Fax: 742-2200 E-mail:	**IDENTIFICACIÓN** C.C. ☒ NIT ☐ C.E. ☐ Otro ☐ Cual _____ Número 80.410.337 TP 57492
4 INVENTOR (ES) (72)	**Nombre:** Deqing LEI, George POLSON, Sonia OBERSON, Ellen M. MEYER, James D KILBY. **Dirección:** 14 Eastgate Lane, Hamden, CT 06514, US; 8295 Old Woods Court, Springboro, OH 45066, US; 44 Tower Lane, Shelton, CT 06484, US; 3287 Chestnut Circle NW, Cleveland, TN 37312, US; 928 Tri Cicle NE, Cleveland, TN 37312, US (Respectivamente). **Nacionalidad o Domicilio:** Estados Unidos de América (Respectivamente).	

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6 Título (54): COMPOSICIÓN DE HIPOCLORITO DE CALCIO RECUBIERTA

7 Clasificación Internacional (51): _____

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US	01-12-2005	60/741,503
US	21-11-2006	11/602,816

9 Comprobante de pago No. 08 - 29 106 **Fecha** 30-05-2008

Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página.

2

10 **ANEXOS**

- [x] Comprobante de pago de la tasa de presentación de la solicitud. $ 501.000
- [x] Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- [x] Poderes, si fuere el caso. **Fotocopia autenticada**
- [ ] Documento de cesión del inventor al solicitante o a su causante.
- [ ] Declaraciones.
- [x] Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- [x] Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- [ ] Copia del examen preliminar efectuado por la IPEA.
- [ ] Traducción del examen preliminar efectuado por la IPEA.
- [ ] De ser el caso, copia del contrato de acceso.
- [ ] De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- [ ] De ser el caso, certificado de depósito del material biológico.
- [ ] Arte final 12x12.
- [ ] De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- [x] Otros: Tarjeta de Propietarios
  Documentos PCT

11 FIGURA CARACTERÍSTICA:

12 Solicito la concesión de la patente.

NOMBRE: JUAN PABLO CADENA SARMIENTO

FIRMA:

C.C. 80.410.337 de Usaquén TP. 57492 del C.S.J.

Instrucciones para la presentación de los anexos, ver reverso de esta página.

AS. 107411

3

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

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

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO DE BOGOTA	062754387	3164836	09/04/2008	17,025,000.00

C O N C E P T O

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

SON: QUINIENTOS UN MIL PESOS

RESPONSABLE : _____

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11/602,816 21 November 2006 (21.11.2006) US

(71) Applicant *(for all designated States except US)*: **ARCH CHEMICALS, INC.** [US/US]; 501 Merritt 7, P.O. Box 5204, Norwalk, CT 06508-5204 (US).

(72) Inventors: **LEI, Deqing**; 14 Eastgate Lane, Hamden, CT 06514 (US). **POLSON, George**; 8295 Old Woods Court, Springboro, OH 45066 (US). **OBERSON, Sonia**; 44 Tower Lane, Shelton, CT 06484 (US). **MEYER, Ellen, M.**; 3287 Chestnut Circle NW, Cleveland, TN 37312 (US). **KILBY, James, D.**; 928 Tri Cicle NE, Cleveland, TN 37312 (US).

(74) Agent: **GARABEDIAN, Todd, E.**; WIGGIN AND DANA LLP, One Century Tower, New Haven, CT 06508-1832 (US).

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

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

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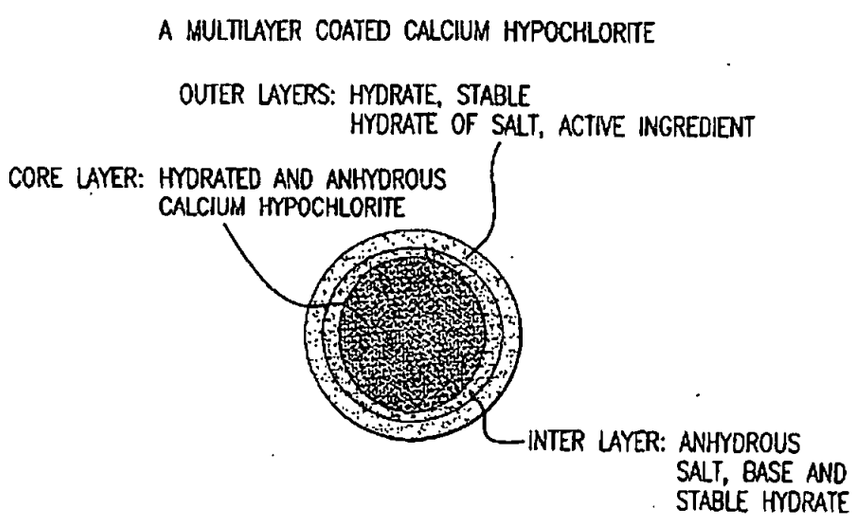
— *with international search report*

[Continued on next page]

(54) Title: COATED CALCIUM HYPOCHLORITE COMPOSITION



(57) Abstract: The present invention is directed to a water treatment composition, comprising: calcium hypochlorite coated with a coating comprising at least one hydrated or anhydrous salt. The present invention is also directed to a water treatment composition, comprising: (a) an inner core layer comprising calcium hypochlorite; (b) one or more interlayers of selected salts positioned on top of said inner core layer, and (c) one or more outer layers o selected salts positioned on top of said interlayer(s).

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 06/45645

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C11D 3/00 (2007.01)
USPC 510/375
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC 510/375

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC 510/375; 423/474; 252/186.36, 252/186.37, 252/187.27, 252/187.28, 252/187.29, 252/187.3 (text search - see terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST (PGPB,USPT,USOC,EPAB,JPAB); Google
Search Terms: calcium hypochlorite, salt, available chlorine, polymeric salt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,201,756 A (Saeman et al.) 06 May 1980 (06.05.1980) Abstract; col 4, ln 10 to col 5, ln 36; col 5, ln 34-36; col 16, ln 44 to col 17, ln 24; col 18, ln 10-59; col 27, ln 5-19	1-7, 10-11, 13-20, 23-26, 28-29 --- 8-9, 12, 21-22 and 27
Y	US 5,164,109 A (Wojtowicz) 17 November 1992 (17.11.1992) col 2, ln 18-46; col 3, ln 6-7; col 4, ln 8-12	8-9, 12, 21-22 and 27
A	US 2004/0214738 A1 (Brennan et al.) 28 October 2004 (28.10.2004) para [0013]-[0015]	1-29

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 June 2007 (03.06.2007)	03 AUG 2007
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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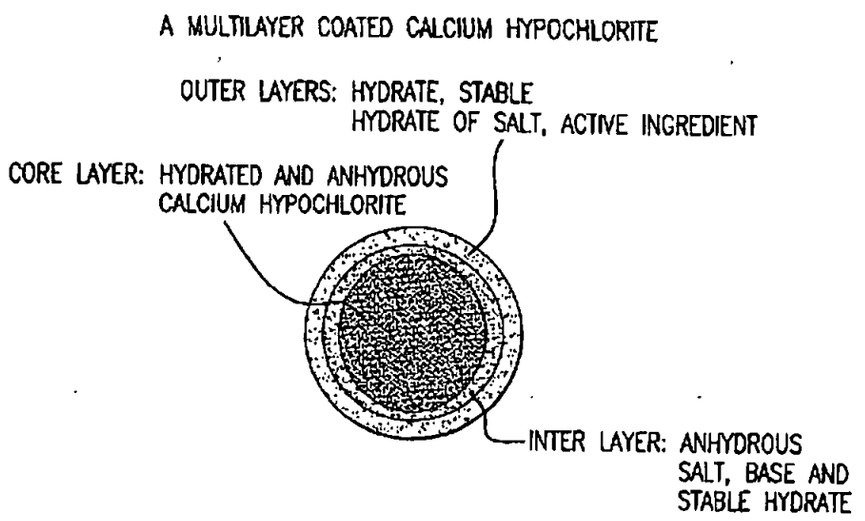
(54) Title: COATED CALCIUM HYPOCHLORITE COMPOSITION



(57) Abstract: The present invention is directed to a water treatment composition, comprising: calcium hypochlorite coated with a coating comprising at least one hydrated or anhydrous salt. The present invention is also directed to a water treatment composition, comprising: (a) an inner core layer comprising calcium hypochlorite; (b) one or more interlayers of selected salts positioned on top of said inner core layer, and (c) one or more outer layers o selected salts positioned on top of said interlayer(s).

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

COATED CALCIUM HYPOCHLORITE COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to coated calcium hypochlorite compositions having low reactivity in handling, storage and transportation. More specifically, this invention relates to a calcium hypochlorite composition coated with one or more hydrated or anhydrous salts. This invention also relates to a calcium hypochlorite composition additionally coated with at least one active water treatment ingredient as a clarifier, scale inhibitor, dispersant, water softener, corrosion inhibitor, algaecide, fungicide, flocculant, binder or mixtures thereof.

2. Brief Description of Art

Hydrated calcium hypochlorite is classified as a Division-5.1 oxidizer as "dangerous goods" for purposes of transport and storage. As a strong oxidizer, hydrated calcium hypochlorite causes a severe increase in burning intensity and burning rate of combustible materials. Thus, the fire of combustible materials in the presence of hydrated calcium hypochlorite can be quite vigorous. Many efforts have been made to produce hydrated calcium hypochlorite containing products that are not classified as a "Division-5.1 oxidizer" as measured by an internationally recognized standard, i.e. the United Nations Protocol: Transport of Dangerous Good: Manual of Tests and Criteria, Section 34; Classification Procedures, Test Methods, and Criteria relating to Oxidizing Substances of Division 5.1.

Another system for classifying oxidizers is given by the National Fire Protection Association (NFPA). In NFPA 430, Code for the Storage of Liquid and Solid Oxidizer (2004 Edition), the definition of an oxidizer is given as any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials and can undergo a vigorous self-sustained decomposition due to contamination or heat exposure. Oxidizers are further broken down according to the degree to which they increase the burning rate of combustible materials as follows:

Class 1: An oxidizer that does not moderately increase the burning rate of combustible materials with which it comes into contact.

Class 2: An oxidizer that causes a moderate increase in the burning rate of combustible materials with which it comes into contact.

Class 3: An oxidizer that causes a severe increase in the burning rate of combustible materials with which it comes into contact.

Class 4: An oxidizer that can undergo an explosive reaction due to contamination or exposure to thermal or physical shock and that causes a severe increase in the burning rate of combustible materials with which it comes into contact.

Calcium hypochlorite is a Class 3 oxidizer according to the NFPA oxidizer classification system.

Recently, US Patent No. 6,638,446 describes a non Division-5.1 calcium hypochlorite composition consisting of a blend of hydrated calcium hypochlorite and magnesium sulfate heptahydrate. In this invention, the blend comprising of 70 part of 68% calcium hypochlorite and 30 part of magnesium sulfate heptahydrate by total weight of the blend, in which the blend contains at least 17% of total water, and 47% available chlorine, is commercially classified as a non Division-5.1 Oxidizer. Similarly, EP 1464617 A2 discloses a non-Division 5.1 oxidizer tablet having the similar composition of hydrated calcium hypochlorite and magnesium sulfate heptahydrate as described in US Patent No. 6,638,446. Although these patents discuss the reduced reactivity of the blends, neither US Patent No. 6,638,446 nor EP 1464617 A2 describes a coated calcium hypochlorite composition.

The approach to coat or encapsulate active hydrated calcium hypochlorite with an inert water-soluble material is well known for the purpose of preventing the contact of calcium hypochlorite and a flammable material and thus to reduce its reactivity and flammability. Several patents have described the processes and coated or encapsulated compositions of hydrated calcium hypochlorite with a variety of coating materials for low reactivity. However, the chemical and physical characterizations of these compositions such as shelf-stability, reactivity, flammability, and Division-5.1 oxidizer classification are not well acknowledged.

For example, the composition disclosed in US Patent No. 3,953,354 describes an encapsulated calcium hypochlorite composition comprising a core hydrated calcium hypochlorite encapsulated with a coating material consisting with about 5 to about 60% of mixture of calcium hypochlorite dihydrate and about 0.1 to about 15% of a water soluble inert inorganic salt such as NaCl and $CaCl_2$ by weight of the granule. The encapsulated

granular product was claimed to resist dusting and caking, and improve retention of its available chlorine on storage. The storage test conducted at 100° C for 2 hours was not indicative of true storage stability due to the extremely high temperature and very short time frame. The potential for self sustaining decomposition was tested by ignition with lighted matches and burning cigarettes, however, no testing was conducted to determine if the samples would increase the burning rate of combustible materials.

US Patent Nos. 4,146,676 and 4,048,351 disclose an encapsulation or coating process comprising granular hydrated calcium hypochlorite coated with about 4-46% of a low melting inorganic salt such as aluminum sulfate hydrate by total weight of the encapsulated calcium hypochlorite. Data are given regarding the storage stability, and several of the examples were evaluated for their sensitivity to decomposition by exposure to localized heating (i.e. lighted cigarette) or chemical contamination (i.e. glycerine), however, no testing was conducted to determine if the samples would increase the burning rate of combustible materials. None of the coated compositions was tested according to the Division-5.1 flame test protocol, or evaluated to see if they would increase the burning rate of combustibles.

The compositions disclosed in US Patent Nos. 4,201,756 and 4,174,411 describe coated calcium hypochlorite with a plurality of layers of inorganic salts which is comprised of chloride, chlorate, nitrate, bromide, bromate, or sulfate salts of Periodic Table Group I alkali metal salts (sodium, potassium, lithium, rubidium, cesium or francium.). The layers of salts form a physical barrier, which was claimed to resist dusting and degradation during handling, and also decreases propensity for ignition and self-sustained decomposition when contacted by a lighted match or incompatible organic materials. However, there is little data to support these claims and no data to show whether any of these compositions is a non Division-5.1 oxidizer or if they increase the burning rate of combustibles.

US Patent No. 4,276,349 described a process for encapsulating calcium hypochlorite that is comprised of a core of calcium hypochlorite encapsulated with a plurality of rounded layers containing a mixture of high percentage of water soluble inorganic salts and calcium hypochlorite. None of the compositions made from the process in the art were specifically characterized and tested for their storage stability and flammability, particularly, according to Division-5.1 Oxidizer classification.

In addition, US Patent Application No. 2003/0038277 A1 and PCT Application WO 03/014013 A2 recently describes a blended or coated calcium hypochlorite process and composition consisting of a polymeric alkali salt and calcium hypochlorite. The composition disclosed in the patent describes an improved environmental stability such as anti-flammability by a brake fluid oil test. However, the actual compositions tested in the arts including contents of available chlorine and moisture were not known and specified, and none of the compositions was tested according to the Division-5.1 flame test protocol, and there is little data to support these claims.

The idea to coat or encapsulate active calcium hypochlorite with an inert water soluble inorganic salt in these prior art references was to reduce the contact of calcium hypochlorite and a flammable material and thus to reduce its reactivity and flammability. The particles with a coating of an inorganic salt as the exterior layer have an increased degree of resistance to ignition by lighted cigarettes or the reaction caused when contacted with organic materials. However, ignition tests are quite different in principle from the above oxidizer classification test and the NFPA classification system which rate the increase in burning rate of combustible materials after ignition has already been initiated. The former is a prevention test of ignition of the material when contact with a lighted match, while the UN oxidizer classification test is to determine the potential to increase the burning rate or the burning intensity of the combustible cellulose when two are thoroughly mixed in a specific ratio, by mass, with the product to cellulose. Since little or no fuel is present in the ignition tests, the procedure does not test the oxidizing properties or the ability to increase the burning rate of combustible materials. Many substances will pass the ignition tests, but will still be classified as Division 5.1 Oxidizers.

One of the examples as described in U.S. Patent No. 4,201,756 was that calcium hypochlorite encapsulated with about 21% of sodium chloride by total weight of the composition prevented ignition of the material when contacted with a lighted match, but it failed to undergo self-sustained decomposition. In contrast, the blend of calcium hypochlorite and sodium chloride by the same weight composition actually accelerate burning, as indicated in US Patent No. 6,638,446.

Therefore, it is difficult to predict whether any compositions in the prior art can be classified as a non Division-5.1 Oxidizer or as NFPA Class 1 or Class 2 oxidizers. Indeed, a coated non Division-5.1, NFPA Class 1 or NFPA Class 2 granular calcium hypochlorite is not seen both in either the marketplace or the literature.

Accordingly, there is an increasing need in this art to produce a calcium hypochlorite product having high available chlorine that is not classified as a Division 5.1 Oxidizer or NFPA Class 3 oxidizer and which has enhanced safety (i.e. diminished fire producing) properties. Therefore, this invention, by providing a solution to that need, is to specifically describe coated calcium hypochlorite compositions with high available chlorine that is not a Division-5.1 oxidizer or NFPA Class 3 oxidizer, that shows excellent storage stability, and has additional advantages for water treatments. These coated calcium hypochlorite compositions are not considered as dangerous goods for transportation and storage, and thus will provide greater public safety.

In addition, the coated calcium hypochlorite composition of the present invention may provide a composition, which is not a non Division-5.1 oxidizer or NFPA Class 3 oxidizer, but with higher available chlorine, lower reactivity and multifunctional benefits than their corresponding blends for water treatments and cleaning applications.

BRIEF SUMMARY OF THE INVENTION

In one aspect, the present invention is directed to a water treatment composition, comprising: calcium hypochlorite coated with a coating comprising at least one hydrated or anhydrous salt; wherein the composition contains about 20 wt% to about 80 wt% available chlorine based on the total weight of the composition, and wherein the composition contains from about 1 wt% to about 50 wt% of hydrated water based on the total weight of the composition, and wherein the coating comprises from about 1% to about 80 wt% of the total weight of the composition, and wherein the composition is classified as a non Division 5.1 oxidizer or as a NFPA Class 1 or NFPA Class 2 oxidizer.

In another aspect, the present invention is directed to a water treatment composition, comprising: (a) an inner core layer comprising calcium hypochlorite; (b) one or more interlayers positioned on top of the inner core layer, the interlayer comprising one or more hydrated or anhydrous inorganic salts, hydrated or anhydrous organic salts, hydrated or anhydrous polymeric salts, alkaline metal hydroxides, alkaline earth hydroxides, and combinations thereof, the interlayer comprising from about 1% to about 80 wt% of the total weight of the composition; and (c) one or more outer layers positioned on top of the interlayer(s), the outer layers comprising at least one hydrated or anhydrous salt, the outer layer comprising from about 1% to about 35 wt% of the total weight of the composition; wherein the composition contains about 20 wt% to about 80 wt% available

chlorine based on the total weight of the composition; wherein the composition contains from about 1 wt% to about 50 wt% of hydrated water based on the total weight of the composition; and wherein the composition is classified as a non Division 5.1 oxidizer or as a NFPA Class 1 or NFPA Class 2 oxidizer.

These and other aspects of the invention will become apparent upon reading the following detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood when taken in conjunction with the following drawings in which:

Figure 1 is a schematic drawing of a multilayer coated calcium hypochlorite embodied by the present invention;

Figure 2 is an elemental map analysis of Sample 3 of the present invention;

Figure 3 is an image of coated Sample 16 of the present invention; and

Figure 4 is an elemental map analysis of coated Sample 16 of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

This invention provides an improved coated granular calcium hypochlorite composition for low reactivity in handling, storage and transportation and treatment of microorganisms in pools, spas, water, and other industrial and recreational water applications. The coated calcium hypochlorite composition of the invention is coated with sufficient amounts of one or more hydrated salts to provide a stable non Division-5.1 oxidizer. The preferred hydrated inorganic salts are alkaline and earth alkaline metal salts of halide, sulfate, phosphate, silicate, borate which is relatively stable for at least one day at about 45°C against their dehydration. The preferred organic and polymeric salts are those alkaline metal salts of organic acid and polymeric acid, and their relatively stable hydrates.

One aspect of this invention is a multilayer coated calcium hypochlorite composition comprising a core of granular calcium hypochlorite coated with one or more hydrated salts. This multilayer coated composition comprises 1) an inner core layer containing hydrated or anhydrous calcium hypochlorite; or a mixture thereof 2) one or more outer layers containing one or more hydrated salts or a mixture thereof; and 3) one or

more interlayers containing either an alkaline or alkaline earth metal hydroxide, an inorganic salt, organic salt or polymeric salt, including hydrated and anhydrous forms such salts, or a mixture thereof. These salt coatings prevent chemical interaction of calcium hypochlorite with the hydrated salt coating materials in the outer layer and thus prevent degradation of calcium hypochlorite.

Another aspect of this invention is to produce coated non Division-5.1 oxidizer composition with high available chlorine, excellent storage stability and multifunctional applications for water and other treatments. The coated calcium hypochlorite composition is not considered as dangerous goods for transportation and storage, and will provide a greater public safety.

An additional aspect of this invention is to produce a coated calcium hypochlorite composition wherein either the outer layers or inner layers of the multilayer composition or the single layer coated composition contains a clarifier, scale inhibitor, dispersant, water softener, corrosion inhibitor, algaecide, fungicide or binder to achieve the desired properties of homogeneity, controlled delivery and multifunctional effects in water and other treatment areas.

The preferred multilayer coated calcium hypochlorite composition may employ specific anhydrous or hydrated salts to achieve a total hydrated water content and available chlorine to reduce its reactivity and burning rate towards an active material such as glycol, cellulose, oil, brake fluid and polymeric materials.

The coated calcium hypochlorite compositions of this invention preferably contain about 20 to about 80% available chlorine and about 1 to about 80% of coating materials, and about 1 to about 50% hydrated water, by total weight of the coated composition.

In addition, the coated calcium hypochlorite composition of the present invention may provide a homogenous composition which is not a non Division 5.1 Oxidizer, but have higher available chlorine, and multifunctional benefits than their corresponding blends for water treatment and other applications.

The term "hydrated salt" as used in the present specification and claims is defined as any hydrated inorganic salt, organic salt, polymeric salt and inorganic base, or a mixture thereof. The term "hydrated" as used in this context is meant to include any such salts or bases that contain one or more waters of hydration, including mixtures of waters of hydration.

The term "hydrated" as used in conjunction with calcium hypochlorite in the present specification and claims refers to calcium hypochlorite that has a water content of at least 5% by weight of the calcium hypochlorite. Preferably, these compositions are commercial "hydrated" (5.5% to 16% water) calcium hypochlorite, CAS number 7778-54-3.

The term "anhydrous" as used in the present specification and claims in conjunction with salts is meant to be any unhydrated, inorganic salt, organic salt, polymeric salt or inorganic base or a mixture thereof. The same term when used in conjunction with calcium hypochlorite, refers to calcium hypochlorite having a water content of less than 5% by weight of the calcium hypochlorite.

In accordance with the present invention, the coated calcium hypochlorite particles with a hydrated or anhydrous salt as the exterior layer are to have an increased degree of resistance to ignition by lighted cigarettes, to reduce the burning rate caused by calcium hypochlorite, and to minimize the reaction caused when contacted with organic materials.

Further in accordance with the present invention, there is provided both singular and multilayer coated granular calcium hypochlorite compositions that may be classified as non Division-5.1 oxidizer, wherein the term "non Division 5.1 Oxidizer composition" as used in the present specification and claims refers to any coated compositions of calcium hypochlorite granules with an hydrated or anhydrous inorganic salt, organic salt, polymeric salt, a base, or their hydrate(s), and a mixture thereof, that is not classified as UN Division 5.1 Oxidizer according to standard testing procedures now in effect. Alternatively, the compositions of the present invention may be classified as either NFPA Class 1 or NFPA Class 2 oxidizers.

In addition, the current UN oxidizer classification test may also be performed to determine the potential of a calcium hypochlorite product for increase in the burning rate or the burning intensity of the combustible cellulose when two are thoroughly mixed in both 1:1 and 4:1 ratios, by mass, with the product to cellulose. Moreover, burn tests may also be performed with the product in contact with combustible materials, such as pails and pouches that may be used as packaging, to determine the potential of a calcium hypochlorite product to increase the burning rate of the combustible materials.

It is commonly recognized that the higher the moisture content of calcium hypochlorite composition, the less stable the calcium hypochlorite is. Therefore, suitable and balanced hydrated moisture content of a coating material should be considered to

provide relatively stable coated calcium hypochlorite composition with high available chlorine.

The coating materials in the present invention includes "inert" and "water soluble" hydrated and anhydrous inorganic salts, organic salts, polymeric salts, and an optional "active ingredients" wherein the term "inert" as defined as little chemical reactivity to calcium hypochlorite that causes severe degradation and higher reactivity, and the term "hydrate" preferably refers to any hydrated salt that contains over 20% hydrated water content. The term "water soluble" is used as solubility of a salt in water from about 5 to about 100%. The term "active ingredients" refers to a known water treatment chemical which are compatible with calcium hypochlorite. In addition, the term "hydrates" in the present invention include a mixture of hydrates of inorganic salts, organic salts, polymeric salts, and an alkaline and alkaline earth metal hydroxides, and a mixture thereof.

The compositions of this invention preferably involve coated granules of calcium hypochlorite containing one or more coatings of an anhydrous or hydrated salt. The calcium hypochlorite granules in the inner core layer of the present invention, typically, have about 54 to about 80% of available chlorine and about 0% to about 12% content of moisture with particle sizes ranging from about 50 to about 4000 microns in diameter. The typical calcium hypochlorite granules in the inner core layer contain anhydrous, hydrated calcium hypochlorite or a mixture thereof.

The singular coated calcium hypochlorite composition of the present invention comprises a singular coating layer that contains one or more hydrated salts or anhydrous forms of the salts, as well as any optional ingredients listed herein.

Typical examples in the present invention include salts that are known to form high hydrated water with over 20% content of hydrated water such as sodium sulfates, lithium metaborate, sodium carbonate, sodium orthophosphate, sodium monohydrogen orthophosphate, sodium phosphate, sodium pyrophosphate, sodium tetraborate, sodium silicate, aluminum sulfate, sodium metasilicate, sodium aluminum sulfate, magnesium sulfate, aluminum potassium sulfate, zinc sulfate, copper sulfate, and sodium citrate and poly(acrylic acid-maleic acid) sodium salt. These salts are most likely to form hydrated salt with high content of hydrated water (waters of hydration) when their aqueous solution is spray dried under the coating conditions.

According to one preferred embodiment of the present invention, the coating material may optionally contain an additional active ingredient for pool, spa and water

treatment, such as water clarifiers, scale inhibitors, water softeners, corrosion inhibitors, algaecides, fungicides, binders, or a mixture thereof. Such ingredients, as well as others, are known to those of skill in the art. Particularly, the additional active ingredient in the present invention includes active ingredient components having known functional properties such as copper sulfate, zinc sulfate, aluminum sulfate, sodium citrate, sodium borate, sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), 1,3-dibromo-5,5dimethylhydrantoin (DBDMH), 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH), 1,3-dichloro-5-ethyl-5-methylhydantoin (DCEMH), 1,3-dibromo-5-ethyl-5-methylhydantoin (DBEMH), 1-bromo-3-chloro-5-methyl-5-ethylhydrantoin (BCEMH), trichloro-, dichloro- and monochlorotriazine, sodium dichloro-s-triazinetrione dichloride, their hydrated form, and a mixture thereof. Amounts of these additional active ingredients preferably range from about 0.1 to about 5 wt%, based on the total weight of the coated composition.

The total content of the coating material in the preferred coated calcium hypochlorite composition in the present invention is from about 1 to about 80 % by weight, and the total available chlorine of the granular calcium hypochlorite is from about 20 to about 80%, based by total weight of the coated calcium hypochlorite compositions. The content of total moisture of the coated granular calcium hypochlorite is about 1% to about 50% based on the total weight of coated calcium hypochlorite composition. The preferred content of hydrated water in the coating material is greater than 15%, preferably, greater than 20% by total weight of coating materials.

The multilayer coated calcium hypochlorite composition in the present invention may comprise at least three layers as shown in Figure 1: 1) a inner core layer containing anhydrous or hydrated calcium hypochlorite granules; 2) an interlayer containing an anhydrous inorganic salt, organic salt, polymeric salt, or an alkaline or alkaline earth base, or its stable hydrate(s), or a mixture thereof, as a protective layer against interfacial interaction of calcium hypochlorite and the coating materials in the outer layers; 3) an outer layer containing a water soluble anhydrous hydrate and hydrated inorganic salt, organic salt or polymeric salt, active water treatment chemicals, or a mixture thereof.

The coating material in the outer layers of the present invention contains at least one anhydrous or hydrated salt as described above for the coating materials in the singular coated calcium hypochlorite. The preferred hydrate of salt that is a hydrate with high

percentage of hydrated water when it is dissolved in water, and then dried under the coating conditions.

More preferably, according to the present invention, the preferred hydrated salt in the outer layer is one that has low heat conductivity, and generates the highest contents of hydrated water by weight of coating material upon coating, and dehydrate all or most of the hydrated water below about 200°C. These salts are most likely to produce a multilayer coated non Divison-5.1 calcium hypochlorite with highest possible available chlorine.

Many inorganic salts and their hydrates are known and available, and are selected for making coating solution to coat granular calcium hypochlorite in the present invention. Typical examples in the present invention include salts that are known to form high hydrated water described as coating materials for the singular layer coated calcium hypochlorite.

Any combination of hydrated or anhydrous salts can be employed to make an aqueous solution for the outer layer coating. A hydrated salt is also made in-situ from the corresponding oxide with the corresponding acid as the coating solution. For example, 20% aqueous magnesium sulfate solution can be made from magnesium oxide and sulfuric acid in about 1:1 molar ratio in the suitable amount of water at room temperature.

The concentration of a salt in coating solution can vary depending on its solubility and viscosity for coating process, and the content in the coating materials, and preferably, a high concentration is applied for more cost considerations. The choices of particular salts are known to those of skill in the art.

In the most preferred embodiment of this invention, the inorganic salts and their hydrates used to generate aqueous solution for outer layers coating include magnesium sulfate, sodium phosphate, sodium pyrophosphate, copper sulfate, a hydrate of these salts, or a mixture thereof. An aqueous solution of such salt or its hydrate produces the solid hydrate or a mixture of the hydrates upon coating depending on the coating conditions.

For example, when the solution made from magnesium sulfate, hydrated forms of magnesium sulfate, such as magnesium sulfate heptahydrate, or from magnesium oxide and sulfuric acid, magnesium sulfate hydrates with hydration number from 3 to 7 under different coating conditions. The coated granular calcium hypochlorite composition with magnesium sulfate tetrahydrate with an average hydrated number of 3-4 provides better storage stability than its higher hydrated forms.

The outer layers of the coated calcium hypochlorite composition according to the present invention also include an anhydrous and/or hydrated alkaline or alkaline earth metal organic salt or polymeric salts. Examples of organic and polymeric salts include a sodium salt of citric acid, benzoic acid, oxalic acid, polyacrylic acid, polymaleic acid, poly(acrylic acid-co-maleic acid), polyepoxysuccinic acid, and its stable hydrates. The polymeric salt generally is a part of the coating materials with a anhydrous and/or hydrated inorganic salt. The content of the polymeric salt is about 0.5 to about 15% by weight of the all coating materials.

The total content of the coating material in the outer layers in a preferred embodiment of the present invention is from about 1 to about 35% by total weight of the coated calcium hypochlorite composition. The total content of the moisture of the coating materials in the outer layers in the present invention is greater than 15%, preferably, greater than 20% by weight of coating materials.

The outer layers of the coated calcium hypochlorite in the present invention may include an active ingredient such as a clarifier, scale inhibitor, water softener, corrosion inhibitor, algaecide, fungicide or binder, or a mixture thereof. The preferred examples are those active ingredients described as an active ingredient in the singular coated granular calcium hypochlorite. Amounts of these additional active ingredients preferably range from about 0.1 to about 5 wt%, based on the total weight of the coated composition.

The interlayer composition in the present invention contains an anhydrous and/or hydrated inorganic salt, organic salt and polymeric salt or an alkaline or alkaline earth metal hydroxide, or a mixture thereof. The alkaline and alkaline earth metal hydroxide, and anhydrous salt, and its hydrate in the interlayer described in the present invention are used as a protective layer from surface-surface interaction of calcium hypochlorite, and the hydrates and other ingredients in the outer layers against loss of chlorine over storage and transportation.

According to the present invention, the interlayer typically contains anhydrous and/or less hydrated alkaline metal chlorides, sulfates, phosphates, silicates or borates, and an alkaline and earth alkaline metal hydroxide. The preferred salt and base are sodium chloride, sodium sulfate, sodium borate, sodium silicate, lithium hydroxide and calcium hydroxide. Components of the interlayer may also be active ingredients.

Calcium hypochlorite decomposes rapidly in the presence of an acid, and is more stable above pH 9. Therefore it is preferred to keep the compositions in the interlayer

from acidic pH ranges. The use of a metal hydroxide in the interlayer is to stabilize calcium hypochlorite against its decomposition by maintaining the basic pH of the coated calcium hypochlorite, and to absorb the chlorine generated during storage. The preferred metal hydroxide is calcium hydroxide.

The content of the coating materials in the interlayer is about 1 to about 80%, preferably, about 3 to about 75% based on total weight of coated calcium hypochlorite composition. The total available chlorine of the multilayer coated calcium hypochlorite is from about 20 to about 80%, and the content of total moisture is about 1 to about 50% by total weight of coated calcium hypochlorite. The thickness of the singular and multilayer coated calcium hypochlorite particles is controlled by particle size of calcium hypochlorite and amount of coating materials used for coatings. Typically, according to the present invention, the thickness of coating is between 10-200 μm.

According to the present invention, SEM and elemental map techniques are used to characterize shape, layer uniformity of coating, EDS is used to determine the thickness of coating, and XRD is used to determine the hydrate form of calcium hypochlorite and salt.

The amount of moisture in the coated calcium hypochlorite may be determined by any standard analytical method for measuring water in calcium hypochlorite and coated calcium hypochlorite compositions. The preferred method is thermo-gravimetric analysis (TGA). The hydrate form of the coating material was also revealed based the weight of moisture contributed to the coating material over the weight of the coating material employed.

The available chlorine of the coated calcium hypochlorite is determined by a standard analytical method used for assay of a typical calcium hypochlorite unless the method is interfered by a coating material.

The coated granular calcium hypochlorite composition in the present invention comprises of about 1 to about 50%, preferably, about 4 to about 30% of the hydrated moisture content, and about 20 to about 80%, preferably about 30% to about 60% available chlorine by weight of the coated calcium hypochlorite granules. The particle sizes of coated granules are in a range from about 40 to about 5,000 μm, preferably about 200 to about 5,000 μm in diameter.

Based on the present invention, the coated granular calcium hypochlorite provides many advantages over the corresponding blend. For example, when the granular calcium hypochlorite containing 68% available chlorine with the particle size of about 200 to about

2000 microns is applied for coating with hydrates of magnesium sulfate, the resulting coated calcium hypochlorite composition contains about 56% available chlorine, about 18% hydrated magnesium sulfate, and less than 14% hydrated moisture by weight of the total coated calcium hypochlorite granules. However, when the calcium hypochlorite is used to blend with magnesium sulfate heptahydrate, the calcium hypochlorite blend contains only about 47% available chlorine, about 30% magnesium sulfate heptahydrate, and about up to 20.4% hydrated moisture by total weight of the blend.

Most importantly, the specifically coated calcium hypochlorite composition in the present invention not only contains higher available chlorine, but also provides excellent stability on elevated temperatures than its corresponding blend.

For example, the coated granular calcium hypochlorite composition containing about 54% available chlorine, about 21% magnesium sulfate hydrates where the majority of the hydrates are magnesium sulfate tetrahydrate, and about 10% hydrated moisture by total weight of the composition is classified as a non Division-5.1 oxidizer with excellent oven stability over 10, 20 and 30 days at 45°C. However, the maximum available chlorine of the calcium hypochlorite blend with magnesium sulfate heptahydrate is only about 47.8% available chlorine, and the oven stability of the blend at 45°C was not good as the coated composition.

In addition, the coated granular calcium hypochlorite composition containing about 47% available chlorine, about 29% magnesium sulfate tetrahydrate, and about 10% hydrated moisture with anhydrous calcium hypochlorite in the inner core layer from the calcium hypochlorite containing 68% available chlorine show the excellent stability with little loss of available chlorine over 30 days at 45 to 50°C.

Similarly, the excellent stability with little loss of available chlorine were observed over 30 days at 45 to 50°C for the coated granular calcium hypochlorite composition wherein the sample consists with about 56% available chlorine, about 28% magnesium sulfate tetrahydrate, and about 10% hydrated moisture with anhydrous calcium hypochlorite in the inner core layer from the calcium hypochlorite with 78% available chlorine. The coated granular calcium hypochlorite is much more stable than the uncoated and their blends with magnesium sulfate heptahydrate.

Additionally, the coated granular calcium hypochlorite in the present invention provides another advantage over the corresponding blend. For example, when the granular calcium hypochlorite containing 68% available chlorine with the particle size of

about 200 to about 2000 microns is coated with hydrates of magnesium sulfate, the resulting coated calcium hypochlorite composition with about 52% available chlorine, and about 9.5% hydrated moisture by weight of the total coated calcium hypochlorite granules is classified as both non Division-5.1 and NAFP-1 oxidizer. However, when the blend of the calcium hypochlorite with magnesium sulfate hydrates containing the same available chlorine and moisture are not non Division-5.1 and NFPA-1 oxidizers.

A coated calcium hypochlorite composition in the present invention is typically produced by a spray fluid bed coater such as Mini-Glatt and GPCG-1 from Glatt Air Technologies, Inc., and ACT 100N and ACT 300Nfrom Applied Chemical Technology, Inc. The variables and conditions of coating are specifically controlled to have minimum wetting on the surface of the calcium hypochlorite particles, and generate suitable mixtures with hydrated salts. A multiple layer coating is accomplished by sequential feeding of deemed coating materials under suitable coating conditions. Coating may be conducted using either a batch or continuous process. Additionally, according to the present invention, a continuous feeding of aqueous coating solution is used to produce a controlled single or multilayer coated granular calcium hypochlorite composition.

The many factors in the coated calcium hypochlorite composition, such as available chlorine, hydrated form, type and heat conductivity of coating materials, stability of the hydrates against its dehydration, total hydrated moisture content, consequential coating layers, are important to reduce its reactivity and burning rate towards an active material such as glycol, cellulose, brake oil, fluid and polymeric materials, and improve its storage stability and performance for water and other treatments.

The coated granular calcium hypochlorite compositions of the present invention are ready for packaging, storage, shipping for use in the treatments of water and the like. Specifically, the coated granules are useful as water treatment sanitizers (e.g. in swimming pools and spas), industrial water treatments, and the like, and are especially safer to transport and store than calcium hypochlorite itself.

According to the present invention, the coated calcium hypochlorite composition is blended in a suitable ratio with other additives including hydrates of inorganic salt, organic salt and polymeric salt, and clarifier, scale inhibitor, flocculants, corrosion inhibitor, algaecide, fungicide and other pool, spa and water treatment additives.

Finally, according to the present invention any shape and forms of calcium hypochlorite including tablets, pellets, briquette, round, irregular, and in any size, can be

coated with the coating materials described above, and provide similar benefits over the corresponding blends.

According to the present invention, the coating technology is suitable for coating other pool, spa, and water treatment actives for low reactivity and better stability in handling, storage and transportation, and for control of microorganisms.

The following examples are further intended to illustrate, but in no way limited, the scope of the present invention. All parts and percentages are by weight and all temperatures are degrees Celsius unless explicitly stated otherwise.

EXAMPLES

The following samples cited in the present invention further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration, and are not to be understood as limitations of the present invention since many variations thereof are possible within the scope.

General Procedures

The moisture and available chlorine analyses were carried out using the standard methods employed for analysis of the uncoated calcium hypochlorite. The flame test method for oxidizing substances described in Section 34 of the United Nations Protocol was used to determine the characteristics of the various coated calcium hypochlorite products described below. The detailed test method is described in the United Nations Recommendations on the Transport of Dangerous Goods; Manual of Tests and Criteria; Third Revised Edition; Section 34 "Classification Procedures, Test Methods and Criteria Relating to Oxidizing Substances of Division 5.1.

For classification, a Non Division-5.1 Oxidizer is a substance which, in both the 4:1 and 1:1 sample-to-cellulose ratios (by mass) tested, does not ignite and burn, or exhibit mean burning times greater than that of a 3:7 mixture (by mass) of potassium bromate and cellulose, where the burning time is taken from when the power is switched on to when the main reaction (e.g. flame, incandescence or glowing combustion) ends.

A medium scale burn testing of packaged granular formulated calcium hypochlorite, packaged salt and empty packaging was used to measure and compare the convective rate of heat release, radiant heat flux, mass loss of the packaged granular

product, packaged salt and empty packaging when exposed to a 46 kW propane fire. The result is used to determine the contribution of the granular oxidizer to the burning rate of typical combustible packaging materials.

The coated calcium hypochlorite in the following examples is typically produced by a spray fluid bed coater such as Mini-Glatt and GPCG-1 from Glatt Air Technologies, Inc., and ACT 100N and ACT 300N from Applied Chemical Technology, Inc., at inlet air temperature of 50-75°C and product temperatures of 35-55°C. A multiple layer coating was accomplished by sequential feeding of coating materials under the conditions at the same or different inlet and product temperatures. The pump rate of a coating solution was specifically controlled to achieve suitable particle wetting and drying to minimize loss of available chlorine. As is known in the art, although these examples were made using a batch process, other processes, such as continuous processes, may also be employed for production of these materials.

EXAMPLE 1: Coated Calcium Hypochlorite Compositions and Classification.

Table 1 tabulates the coated calcium hypochlorite compositions of the samples 1-10 including type of calcium hypochlorite, available chlorine and composition, coating material and moisture, and Division-5.1 classification. The composition of the starting uncoated calcium hypochlorite contained about 68% available chlorine, about 6.6% moisture with typical particle size in the range of 200-2000 μm in diameter. In Table 1, Samples 1 to 9 include calcium hypochlorite: 68% available chlorine, particle size: ~200-2000 μm with ~6.6% moisture; Sample 10 includes calcium hypochlorite: 78% available chlorine, particle size: ~100-2000 μm with ~10.2% moisture, was used for coating. Percentages of ingredients refer to weight percents.

Table 1 Composition Of The Coated Granular Calcium Hypochlorite And Classification

Sample #	Coated Calcium Hypochlorite Granules Composition				AvCl ** (%)	Moisture (%)	Non Division-5.1
	Core layer	1st layer	2nd layer	3rd layer			
1	77.3% $Ca(OCl)_2 \cdot xH_2O$	0.7% NaOH	22.0% $MgSO4 \cdot xH_2O$	-	52.2	17.1	Yes
2	83.4% $Ca(OCl)_2 \cdot xH_2O$	0.7% NaOH	13.4% $MgSO_4\ xH_2O$	2.5% poly(AM) $Na \cdot nH_2O$*	55.9	13.8	Yes
3	82.0% $Ca(OCl)_2 \cdot xH_2O$	1.8% NaCl	16.2% $MgSO_4\ xH_2O$	-	55.0	14.0	Yes

4	81.5% $Ca(OCl)_2 \cdot xH_2O$	1.6% $Ca(O)_2$	16.9% $MgSO_4 \cdot xH_2O$	-	51.3	15.0	Yes
5	80.7% $Ca(OCl)_2 \cdot xH_2O$	-	19.3% $MgSO_4 \cdot xH_2O$	-	54.7	10.9	Yes
6	74.3% $Ca(OCl)_2 \cdot xH_2O$	1.5% NaCl	24.2% $MgSO_4 \cdot xH_2O$	-	50.9	8.7	Yes
7	80.5% $Ca(OCl)_2 \cdot xH_2O$	-	19.5% $MgSO_4 \cdot xH_2O$	-	54.4	9.2	Yes
8	73.6% $Ca(OCl)_2$ xH_2O	-	26.4% $MgSO_4$ xH_2O	-	50.8	9.6	Yes
9	69% $Ca(OCl)_2 \cdot xH_2O$	-	31% $MgSO_4 \cdot xH_2O$	-	47.2	10.2	Yes
10	72% $Ca(OCl)_2 \cdot xH_2O$	-	28% $MgSO_4 \cdot xH_2O$	-	56.1	10.4	Yes

* Poly(AM)Na: poly(acrylic acid-co-maleic acid) sodium salt; ** AvCl: Available chlorine

XRD analysis of samples 5 to 8 indicates that the calcium hypochlorite in the inner core layer consists with a mixture of about 70% anhydrous and about 30% hydrated calcium hypochlorite where the uncoated calcium hypochlorite contains at least 70% hydrated form of calcium hypochlorite, and the inner core layer of the samples 9 and 10 contain almost all anhydrous calcium hypochlorite. XRD analysis of the magnesium sulfate hydrate in the outer layer showed that the majority is its tetrahydrate. The wet analysis of the moisture of the coated samples 1 to 4 indicates that hydrates of magnesium sulfate in the composition contain an average hydrated water of about 6.

As data in Table 2 indicate, the coated samples 6 to 8 show similar oven stability as the uncoated calcium hypochlorite at 45°C over 10, 20 and 30 days, which is believed to be simulated as 1, 2 and 3 years of storage time under ordinary storage conditions. Surprisingly, the coated samples 9 and 10 show the excellent stability over 30 days at 45°C. Little loss of available chlorine was observed.

Table 2. Oven Stability Of Coated vs.Uncoated Calcium Hypochlorite At 45°C

Sample	AvCl % After 0 day	AvCl loss % after 10 days	AvCl loss After 20 days	AvCl loss after 30 days
uncoated	69.2	2.9	8.7	15.9

5	54.5	4.4	16.3	26.4
6	50.9	3.5	7.0	12.7
7	54.4	4.6	8.6	16.7
8	50.8	-0.18	7.5	11.8
9	47.2	-1.3	-0.09	-1.54
10	56.1	-0.3	1.0	3.3

Table 3 tabulates the comparison of example 7and the corresponding blend including type of calcium hypochlorite, available chlorine, composition, coating material and moisture against their Division-5.1 classification. The composition of the starting uncoated calcium hypochlorite contained 69% available chlorine, about 9.2% moisture with an average particle size in the range of 200-2000 μm in diameter.

Table 3. Composition Of The Coated Granular Calcium Hypochlorite And Classification (Calcium hypochlorite: ~78% AvCl with particle size ~100 to 2000 μm in Samples 11 and 8)

Sample ID	Coating material and its content in the coated product		AvCl (%)	Moisture (%)	Non Division-5.1
	Core calcium hypochlorite	outer layer			
7	80.5%	19.5%$MgSO_4 \cdot xH_2O$	54.4	9.2	yes
80/20 blend of calcium hypochlorite/ $MgSO_4 \cdot 7H_2O$			54.5	15.3	NO

As shown in Table 3, the blended sample with magnesium sulfate heptahydrate having the same available chlorine as the coated sample 7 is not a non Division-5.1 oxidizer.

Table 4 show some benefits of the coated calcium hypochlorite composition vs. the corresponding blends over available chlorine and Division-5.1 classification. In Table 4, samples 2 and 11 contain calcium hypochlorite ~68% AvCl, particle size: ~200-2000 μm. Samples 12 and 13 contain ~78% AvCl with particle size ~100 to 2000.

Table 4. Comparison of blend and coated Non Division-5.1 oxidizers

Sample #	Coated Calcium Hypochlorite Granules Composition			AvCl (%)	Moisture (%)	Non Division-5.1
	method	$Ca(OCl)_2 \cdot xH_2O$	Coating material			
11	blending	70%	30% $MgSO_4 \cdot 7H_2O$	47.6	19.6	Yes
2	coating	83%	0.7% NaOH + 14% $MgSO_4 \cdot xH_2O$ +2.5% poly(AM) $Na \cdot xH_2O$	55.9	13.8	Yes
12	blending	70%	30% $MgSO_4 \cdot 7H_2O$	54.4	24.1	Yes
13	coating	75%	0.6% NaOH + 25% $MgSO_4 \cdot xH_2O$	57.7	19.7	Yes

The results in Tables 4 demonstrate that the coated non Division-5.1 samples 2 and 13 provide higher available chlorine than the corresponding blended Division-5.1 samples 11 and 12 even where the moisture contents of the coated samples are much lower than the corresponding blended sample.

Table 5 shows the relative burning time benefits of other samples coated with other coating materials vs. their corresponding blends. Longer burning times were observed from the coated calcium hypochlorite compositions based on similar available chlorine and the same components used as coating materials although the moisture contents in the coated samples are lower than their blends. In Table 5, each sample contains calcium hypochlorite: 68% available chlorine, particle size: ~200-2000 μm with ~6.6% moisture.

Table 5. Comparison Of Blend And Coated Calcium Hypochlorite Composition

Sample #	Coated calcium hypochlorite granules composition			AvCl (%)	Moisture (%)	Burning time (sec)
	method	$Ca(OCl)_2 \cdot H_2O$	Coating material			
14	blend	80%	20% $MgSO_4 \cdot xH_2O$	54.0	16.2	84
15	coating		0.4% NaOH + 16% $MgSO_4 \cdot xH_2O$	56.1	13.0	100
16	blending	80%	20% Na_3PO_4-$12H_2O$	54.0	16.2	62
17	coating	83%	17% Na_3PO_4-$12H_2O$	55.4	14.1	83
18	coating	82%	3% $Na_3PO_4 \cdot yH_2O$ + 6% $MgSO_4 \cdot xH_2O$ + 9% $CuSO_4 \cdot zH_2O$	54.7	12.2	81
19	coating	83%	15% $Na_3PO_4 \cdot yH_2O$ + 2% poly(AM)Na·nH_2O*	55.7	13.7	90

*poly(AM)Na·nH_2O: poly(acrylic acid-co-maleic acid) sodium·nH2O

For example, the sample 15, coated with magnesium sulfate hydrate, shows 19% longer burning time than the blended sample 14 with magnesium sulfate heptahydrate wherein the coated sample 15 even has higher available chlorine and lower hydrated moisture. Similarly, 34% longer burning time was observed from the coated sample 17 vs. the blended sample 16 with sodium phosphate dodecahydrate.

In addition, more than 30% longer burning time was observed from the multilayer coated sample 18 with hydrates of sodium phosphate, magnesium sulfate and copper

sulfate, and the sample 19 with hydrates of sodium phosphate and poly(AM)Na vs. the blend sample 16 with sodium phosphate dodecahydrate.

SEM, EDS and XRD analyses, and the elemental map techniques are particularly employed for characterization of features of coated samples.

Figure 2 shows the elemental map analysis of the coated sample 3, and demonstrates the multilayer uniform coating of the particles with calcium hypochlorite in the inner core layer, sodium chloride in the interlayer and magnesium sulfate hydrates in the outer layer.

The SEM and EDS analyses also demonstrate the multilayer coating of sample 18, as shown in Figure 3 and 4. Figure 4 shows that sample 18 is coated with magnesium sulfate hydrates in the interlayer and copper sulfate hydrates in the outer layer. Microscopic image and EDS analysis of the coating via cross section of the cut particles was revealing as shown in Figures 3 and 4. The coating shown with a blue color material in Figure 3 is copper sulfate hydrate, and is about 25μm thick over about 1 mm diameter particle. The elemental map analysis shows clearly two layers with magnesium sulfate hydrates in the interlayer and copper sulfate hydrates in the outer layer. The copper sulfate hydrate coating was shown to be rather uniform and around 15-20 μm thick, while magnesium sulfate hydrate coating was the more variable and thinner coating with about 7-15 μm thick.

While the present invention is primarily directed to having anhydrous or hydrated calcium hypochlorite as the core materials and hydrated salts as the coating material, the invention may also encompass other embodiments where the above-noted active ingredients are part of or all of the core material. Preferably, other sanitizing oxidizers such as trichloroisocyanuric acid (TCCA) sodium dichloroisocyanurate (SDCC), and chloro and bromo hydantoins as well as mixtures of sanitizing oxidizers may be useful as such alternative core material. Moreover, other coating materials such as organo-metallics could be used as alternative coating materials instead of the above-noted salt materials. Furthermore, the present invention also encompasses the use of other well known coating techniques such as the use of core-shell particles to make the coated compositions. The composition of such core-shell particles could vary from 10% average chlorine (AvCl) content up to 80% average chlorine (AvCl) content.

While the invention has been described above with reference to specific embodiments thereof, it is apparent that many changes, modifications, and variations can

be made without departing from the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims.

WHAT IS CLAIMED IS:

1. A water treatment composition, comprising:

calcium hypochlorite coated with a coating comprising at least one hydrated or anhydrous salt;

wherein said composition contains about 20 wt% to about 80 wt% available chlorine based on the total weight of said composition, and

wherein said composition contains from about 1 wt% to about 50 wt% of hydrated water based on the total weight of said composition, and

wherein said coating comprises from about 1% to about 80 wt% of the total weight of said composition, and

wherein said composition is classified as a non Division 5.1 oxidizer or as a NFPA Class 1 or NFPA Class 2 oxidizer.

2. The water treatment composition of claim 1, wherein said calcium hypochlorite contains from about 0 wt% to about 12 wt% of water, based on the total weight of said calcium hypochlorite.

3. The water treatment composition of claim 1, wherein said calcium hypochlorite is a particle having a diameter ranging from about 40 to about 5000 microns.

4. The water treatment composition of claim 3, wherein said calcium hypochlorite is a particle having a diameter ranging from about 200 to about 5000 microns.

5. The water treatment composition of claim 1, wherein said salt is selected from the group consisting of hydrated or anhydrous inorganic salts, hydrated or anhydrous organic salts, hydrated or anhydrous polymeric salts, and combinations thereof.

6. The water treatment composition of claim 5, wherein said hydrated salt is selected from the group consisting of alkaline and alkaline earth metal salts of halides, alkaline and alkaline earth metal salts of sulfate, alkaline and alkaline earth metal salts of phosphate, alkaline and alkaline earth metal salts of silicate, alkaline and alkaline earth metal salts of borate, alkaline and alkaline earth metal hydroxides, and combinations thereof.

7. The water treatment composition of claim 5, wherein said hydrated salt is selected from the group consisting of sodium sulfates, lithium metaborate, sodium carbonate, sodium orthophosphate, sodium monohydrogen orthophosphate, sodium phosphate, sodium pyrophosphate, sodium tetraborate, sodium silicate, aluminum sulfate, sodium metasilicate, sodium aluminum sulfate, magnesium sulfate, aluminum potassium sulfate, zinc sulfate, copper sulfate, sodium citrate, poly(acrylic acid-maleic acid) sodium salt, and combinations thereof.

8. The water treatment composition of claim 1, wherein said coating further comprises one or more additional ingredients selected from the group consisting of water clarifiers, scale inhibitors, dispersants, water softeners, corrosion inhibitors, algaecides, fungicides, binders, and combinations thereof, and wherein said additional ingredients are present in an amount ranging from 0.1 to 5 wt%, based on the total weight of the coated composition.

9. The water treatment composition of claim 8, wherein said additional ingredients are selected from the group consisting of copper sulfate, zinc sulfate, aluminum sulfate, sodium citrate, sodium borate, sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), 1,3-dibromo-5,5dimethylhydrantoin (DBDMH), 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH), 1,3-dichloro-5-ethyl-5-methylhydantoin (DCEMH), 1,3-dibromo-5-ethyl-5-methylhydantoin (DBEMH), 1-bromo-3-chloro-5-methyl-5-ethylhydrantoin (BCEMH), trichloro-, dichloro- and monochlorotriazine, sodium dichloro-s-triazinetrione dichloride, their hydrated form, and combinations thereof.

10. The water treatment composition of claim 1, wherein said composition contains about 30 wt% to about 60 wt% available chlorine, based on the total weight of said composition.

11. The water treatment composition of claim 1, wherein said composition contains from about 4 wt% to about 30 wt% of hydrated water based on the total weight of said composition.

12. The water treatment composition of claim 1, wherein said composition is formed into a tablet or briquette.

13. The water treatment composition of claim 1, wherein said salt is magnesium sulfate tetrahydrate.

14. A water treatment composition, comprising:

(a) an inner core layer comprising calcium hypochlorite;

(b) one or more interlayers positioned on top of said inner core layer, said interlayer comprising one or more hydrated or anhydrous inorganic salts, hydrated or anhydrous organic salts, hydrated or anhydrous polymeric salts, alkaline metal hydroxides, alkaline earth hydroxides, and combinations thereof, said interlayer comprising from about 1% to about 80 wt% of the total weight of said composition; and

(c) one or more outer layers positioned on top of said interlayer(s), said outer layers comprising at least one hydrated or anhydrous salt, said outer layer comprising from about 1% to about 35 wt% of the total weight of said composition;

wherein said composition contains about 20 wt% to about 80 wt% available chlorine based on the total weight of said composition;

wherein said composition contains from about 1 wt% to about 50 wt% of hydrated water based on the total weight of said composition;

and wherein said composition is classified as a non Division 5.1 oxidizer or as a NFPA Class 1 or NFPA Class 2 oxidizer.

15. The water treatment composition of claim 14, wherein said calcium hypochlorite contains from about 0 wt% to about 12 wt% of water, based on the total weight of said calcium hypochlorite.

16. The water treatment composition of claim 14, wherein said calcium hypochlorite is a particle having a diameter ranging from about 40 to about 5000 microns.

17. The water treatment composition of claim 16, wherein said calcium hypochlorite is a particle having a diameter ranging from about 200 to about 5000 microns.

18. The water treatment composition of claim 14, wherein hydrated or anhydrous salt in said outer layer is selected from the group consisting of hydrated or anhydrous inorganic salts, hydrated or anhydrous organic salts, hydrated or anhydrous polymeric salts, and combinations thereof.

19. The water treatment composition of claim 18, wherein said hydrated salt is selected from the group consisting of alkaline and alkaline earth metal salts of halides, alkaline and alkaline earth metal salts of sulfate, alkaline and alkaline earth metal salts of phosphate, alkaline and alkaline earth metal salts of silicate, alkaline and alkaline earth metal salts of borate, alkaline and alkaline earth metal hydroxides, and combinations thereof.

20. The water treatment composition of claim 18, wherein said hydrated salt is selected from the group consisting of sodium sulfates, lithium metaborate, sodium carbonate, sodium orthophosphate, sodium monohydrogen orthophosphate, sodium phosphate, sodium pyrophosphate, sodium tetraborate, sodium silicate, aluminum sulfate, sodium metasilicate, sodium aluminum sulfate, magnesium sulfate, aluminum potassium sulfate, zinc sulfate, copper sulfate, sodium citrate, poly(acrylic acid-maleic acid) sodium salt, and combinations thereof.

21. The water treatment composition of claim 14, wherein said one or more outer layers further comprise one or more additional ingredients selected from the group consisting of water clarifiers, scale inhibitors, dispersants, water softeners, corrosion inhibitors, algaecides, fungicides, binders, and combinations thereof, and wherein said additional ingredients are present in an amount ranging from 0.1 to 5 wt%, based on the total weight of the coated composition.

22. The water treatment composition of claim 21, wherein said outer layer further comprises one or more additional agents selected from the group consisting of copper sulfate, zinc sulfate, aluminum sulfate, sodium citrate, sodium borate, sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), 1,3-dibromo-5,5dimethylhydantoin (DBDMH), 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH), 1,3-dichloro-5-ethyl-5-methylhydantoin (DCEMH), 1,3-dibromo-5-ethyl-5-methylhydantoin (DBEMH), 1-bromo-3-chloro-5-

methyl-5-ethylhydrantoin (BCEMH), trichloro-, dichloro- and monochlorotriazine, sodium dichloro-s-triazinetrione dichloride, their hydrated form, and combinations thereof, and wherein said additional ingredients are present in an amount ranging from 0.1 to 5 wt%, based on the total weight of the coated composition..

23. The water treatment composition of claim 14, wherein said inorganic salt in said interlayer comprises alkaline metal chlorides, alkaline metal sulfates, alkaline metal phosphates, alkaline metal silicates, alkaline metal borates, and combinations thereof.

24. The water treatment composition of claim 14, wherein interlayer is a salt selected from the group consisting of sodium chloride, sodium sulfate, sodium borate, sodium silicate, lithium hydroxide, calcium hydroxide, and combinations thereof.

25. The water treatment composition of claim 14, wherein said composition contains about 30 wt% to about 60 wt% available chlorine, based on the total weight of said composition.

26. The water treatment composition of claim 14, wherein said composition contains from about 4 wt% to about 30 wt% of hydrated water based on the total weight of said composition.

27. The water treatment composition of claim 14, wherein said composition is formed into a tablet or briquette.

28. The water treatment composition of claim 14, wherein said salt is magnesium sulfate tetrahydrate.

29. The water treatment composition of claim 14, wherein said outer layer comprises a polymeric salt comprising from about 0.5% to about 15 wt% of the total weight of said composition.

A MULTILAYER COATED CALCIUM HYPOCHLORITE

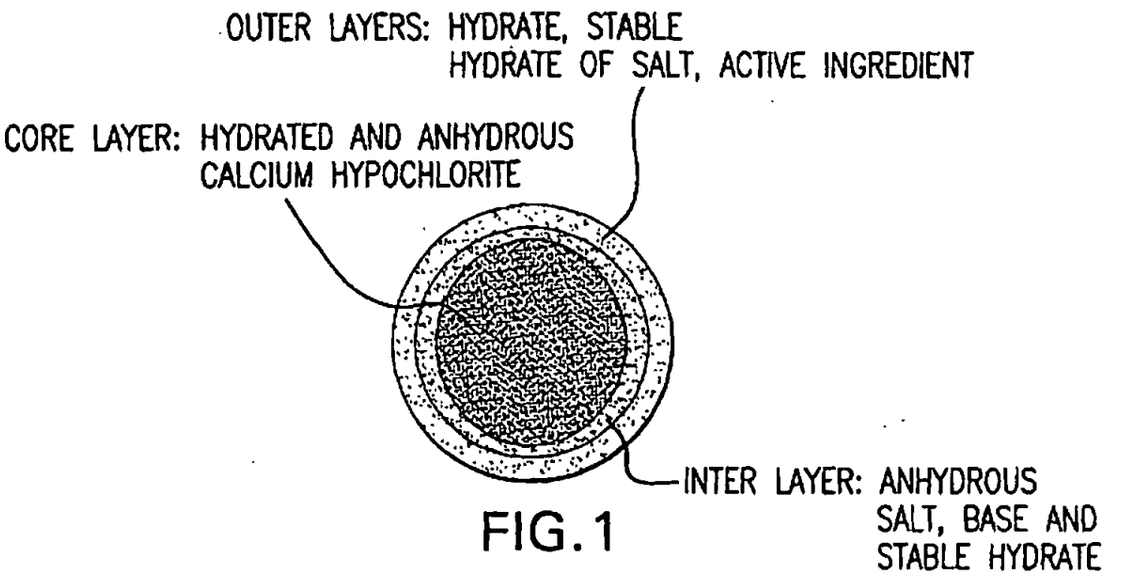

FIG. 1

ELEMENTAL MAP ANALYSIS OF COATED SAMPLE 3

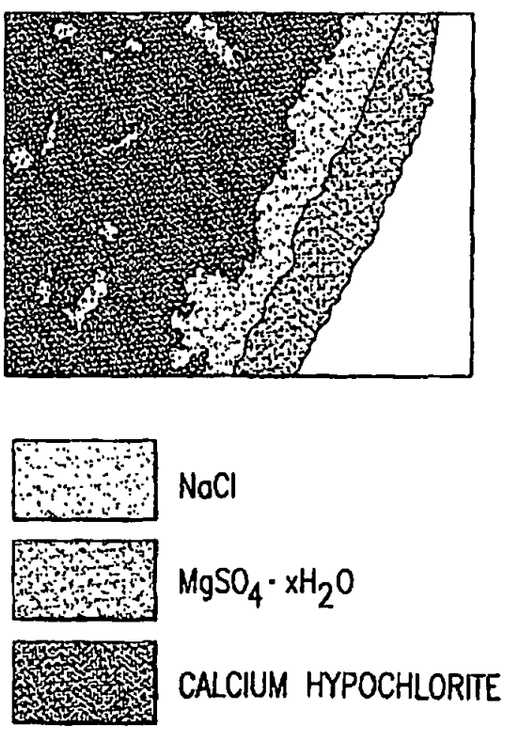

FIG. 2

IMAGE OF THE COATED SAMPLE 16

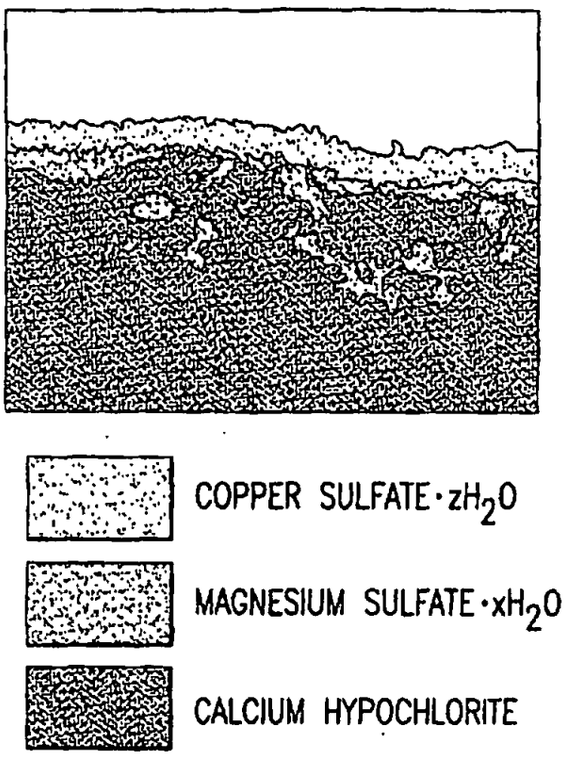

FIG.3

ELEMENTAL MAP ANALYSIS
OF THE COATED SAMPLE 16

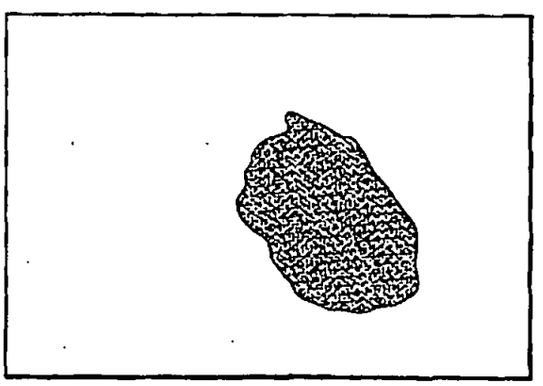

FIG.4

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(81) Países designados *(a menos que se indique lo contrario para cada clase de protección disponible)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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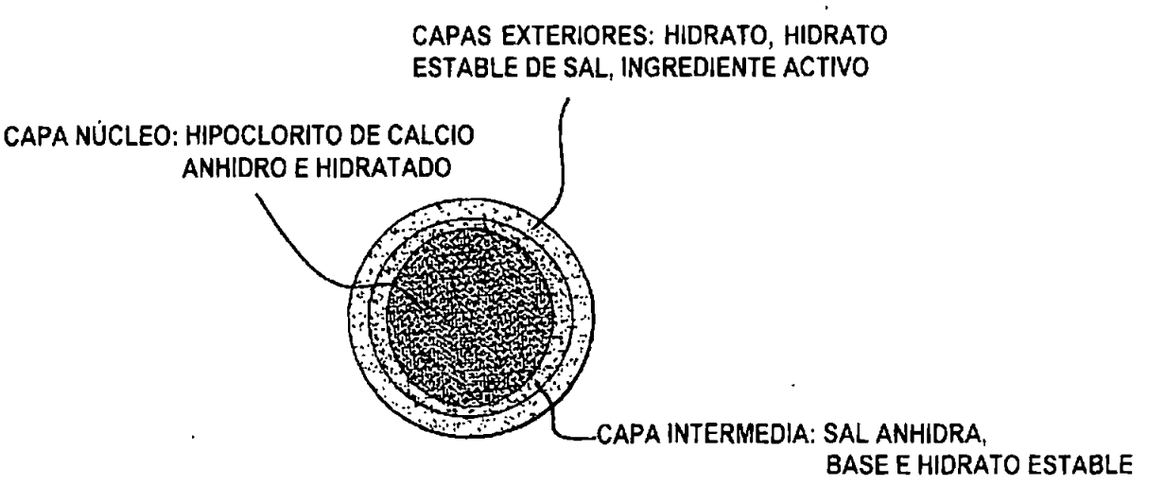
[Continúa en la página siguiente]

(54) **Título:** COMPOSICIÓN DE HIPOCLORITO DE CALCIO RECUBIERTA



(57) **Extracto:** La presente invención se dirige a una composición para tratamiento de agua, que contiene: hipoclorito de calcio recubierto con un recubrimiento que incluye por lo menos una sal anhidra o hidratada. La presente invención se dirige igualmente a una composición para tratamiento de agua, que contiene: (a) una capa núcleo interior que incluye hipoclorito de calcio; (b) una o más capas intermedias de sales seleccionadas, situadas en la parte superior de la citada capa núcleo interior, y (c) una o más capas exteriores de salos seleccionadas, situadas en la parte superior de la(s) citada(s) capa(s) intermedia(s).

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Para códigos de dos letras y otras abreviaturas, remítase a las "Notas Guía sobre Códigos y Abreviaturas" que aparece al comienzo de cada edición regular del Boletín Oficial PCT.

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COMPOSICIÓN DE HIPOCLORITO DE CALCIO RECUBIERTA

ANTECEDENTES DE LA INVENCIÓN

1. Campo de la Invención

Esta invención se refiere a composiciones de hipoclorito de calcio recubiertas, que tienen baja reactividad en la manipulación, almacenamiento y transporte. Más específicamente, esta invención se refiere a una composición de hipoclorito de calcio recubierta con una o más sales anhidras o hidratadas. Esta invención se relaciona igualmente con una composición de hipoclorito de calcio, recubierta adicionalmente con por lo menos un ingrediente activo para el tratamiento de agua como un purificador, inhibidor de costra de óxido, dispersante, suavizante de agua, inhibidor de la corrosión, alguicida, fungicida, floculante, aglutinante o sus mezclas.

2. Breve Descripción del Arte

El hipoclorito de calcio hidratado, como oxidante incluido en la División 5.1, se clasifica como "mercancía peligrosa" para efectos de transporte y almacenamiento. Como oxidante fuerte, el hipoclorito de calcio hidratado ocasiona un serio aumento en la intensidad de combustión y la velocidad de combustión de materiales combustibles. Por consiguiente, el fuego de materiales combustibles en la presencia de hipoclorito de calcio hidratado puede ser muy vigoroso. Se han hecho muchos esfuerzos para producir hipoclorito de calcio hidratado que contenga productos no clasificados como un "oxidante incluido en la División 5.1", medidos por una norma reconocida internacionalmente, es decir, el Protocolo de las Naciones Unidas: Transporte de Mercancías Peligrosas: Manual de Ensayos y Criterios, Sección 34; Procedimientos de Clasificación, Métodos de Ensayo y Criterios Relativos a Sustancias Oxidantes de la División 5.1.

Otro sistema para clasificar oxidantes lo especifica la Asociación Nacional de Protección de Incendios (NFPA, en inglés). En NFPA 430,

Código para el Almacenamiento de Oxidantes Líquidos y Sólidos (Edición 2004), se incluye la definición de un oxidante como cualquier material que fácilmente desprende oxígeno u otro gas oxidante, o que reacciona fácilmente para promover o iniciar la combustión de materiales combustibles y que puede experimentar una descomposición auto-sostenida vigorosa, debida a la contaminación o exposición al calor. Los oxidantes se sub-clasifican de acuerdo con el grado, en el cual aumentan la velocidad de combustión de materiales combustibles, en la siguiente forma:

Clase 1: Un oxidante que no aumenta moderadamente la velocidad de combustión de materiales combustibles, con los cuales entra en contacto.

Clase 2: Un oxidante que causa un aumento moderado en la velocidad de combustión de materiales combustibles, con los cuales entra en contacto.

Clase 3: Un oxidante que ocasiona un aumento serio en la velocidad de combustión de materiales combustibles, con los cuales entra en contacto.

Clase 4: Un oxidante que experimenta una reacción explosiva debida a la contaminación o exposición a choque físico o térmico y que produce un aumento serio en la velocidad de combustión de materiales combustibles, con los cuales entra en contacto.

El hipoclorito de calcio es un oxidante Clase 3 de acuerdo con el sistema de clasificación de oxidantes de la NFPA.

Recientemente, la Patente de los Estados Unidos No. 6,638,446 describe una composición de hipoclorito de calcio no incluida en la División 5.1, compuesta de una mezcla de hipoclorito de calcio hidratado y heptahidrato de sulfato de magnesio. En esta invención, la mezcla conformada por 70 partes de 68% de hipoclorito de calcio y 30 partes de heptahidrato de sulfato de magnesio en peso total de la mezcla, en la cual [invención] la mezcla contiene por lo menos 17% de agua total y 47% de cloro disponible, se clasifica comercialmente como un oxidante no incluido en la División 5.1. Análogamente, la EP 1464617 A2 divulga una tableta de oxidante no incluido en la División 5.1, que tiene una composición similar de hipoclorito de calcio hidratado y heptahidrato de sulfato de magnesio,

como se describe en la Patente de los Estados Unidos No. 6,638,446. Aunque estas patentes discuten la reactividad reducida de las mezclas, ni la Patente de los Estados Unidos No. 6,638,446 ni la EP 1464617 A2 describen una composición de hipoclorito de calcio recubierta.

El método de recubrir o encapsular hipoclorito de calcio hidratado activo con un material hidrosoluble inerte es bien conocido para el propósito de evitar el contacto de hipoclorito de calcio y un material inflamable y, en consecuencia, de reducir su reactividad e inflamabilidad. Varias patentes han descrito los procesos y composiciones encapsuladas o recubiertas de hipoclorito de calcio hidratado con una variedad de materiales de recubrimiento para una reactividad baja. No obstante, no son bien reconocidas las caracterizaciones físicas y químicas de estas composiciones tales como estabilidad durante el almacenamiento, reactividad, inflamabilidad y la clasificación como oxidante incluido en la División 5.1.

Por ejemplo, la composición divulgada en la Patente de los Estados Unidos No. 3,953,354 describe una composición de hipoclorito de calcio encapsulada que comprende un núcleo de hipoclorito de calcio hidratado encapsulado con un material de recubrimiento que consta de alrededor de 5 a alrededor de 60% de una mezcla de dihidrato de hipocorito de calcio y alrededor de 0.1 a alrededor de 15% de una sal inorgánica inerte hidrosoluble tal como NaCl y $CaCl_2$ en peso del gránulo. Se reivindicaba que el producto granular encapsulado era resistente a la generación de polvo y al apelmazamiento, y mejoraba la retención de su cloro disponible al almacenarlo. El ensayo de almacenamiento, llevado a cabo a 100°C durante 2 horas, no fue indicativo de una verdadera estabilidad al almacenamiento, debido a la temperatura extremadamente elevada y al marco cronológico muy corto. El potencial de descomposición auto-sostenida se ensayó mediante ignición con fósforos encendidos y cigarrillos prendidos; no obstante, no se realizaron experimentos para determinar si las muestras aumentarían la velocidad de combustión de materiales combustibles.

Las Patentes de los Estados Unidos No. 4,146,676 y 4,048,351 divulgan un proceso de encapsulamiento o recubrimiento que incluye hipoclorito de calcio hidratado granular, recubierto con alrededor de 4-46% de una sal inorgánica con bajo punto de fusión, tal como hidrato de sulfato de aluminio en peso total del hipoclorito de calcio encapsulado. Los datos se dan con respecto a la estabilidad al almacenamiento, y varios de los ejemplos se evaluaron con respecto a su sensibilidad a la descomposición por exposición a calentamiento localizado (es decir, un cigarrillo prendido) o contaminación química (es decir, glicerina); sin embargo, no se realizaron experimentos para determinar si las muestras aumentarían la velocidad de combustión de materiales combustibles. Ninguna de las composiciones recubiertas se ensayó de acuerdo con el protocolo de ensayo a la llama de la División 5.1, o se evaluó para ver si incrementarían la velocidad de combustión de combustibles.

Las composiciones divulgadas en las Patentes de los Estados Unidos No. 4,201,756 y 4,174,411 describen hipoclorito de calcio recubierto con una pluralidad de capas de sales inorgánicas, que se componen de sales cloruro, clorato, nitrato, bromuro, bromato, o sulfato de metales alcalinos del Grupo 1 de la Tabla Periódica (sodio, potasio, litio, rubidio, cesio o francio). Las capas de sales forman una barrera física, reivindicada para contrarrestar la generación de polvo y la degradación durante la manipulación, y que disminuye además la propensión a la ignición y la descomposición auto-sostenida, cuando se pone en contacto con un fósforo encendido o materiales orgánicos incompatibles. No obstante, existen pocos datos para sustentar estas reivindicaciones y se carece de información para demostrar si cualquiera de estas composiciones es un oxidante no incluido en la División 5.1 o si no aumentan la velocidad de combustión de combustibles.

La Patente de los Estados Unidos No. 4,276,349 describió un proceso para encapsular hipoclorito de calcio, compuesto de un núcleo de hipoclorito de calcio encapsulado con una pluralidad de capas redondas que contienen una mezcla de un alto porcentaje de sales inorgánicas

hidrosolubles e hipoclorito de calcio. Ninguna de las composiciones elaboradas a partir de los procesos en el arte se caracterizó específicamente y se ensayó con respecto a su estabilidad al almacenamiento e inflamabilidad, particularmente, de acuerdo con la clasificación de Oxidantes incluidos en la División 5.1.

Además, la Solicitud de Patente de los Estados Unidos No. 2003/0038277 A1 y la Solicitud PCT WO 03/014013 A2 describen recientemente un proceso [para la fabricación] de un hipoclorito de calcio recubierto o mezclado y una composición, compuesta de una sal alcalina polimérica e hipoclorito de calcio. La composición divulgada en la patente describe una estabilidad ambiental mejorada, tal como anti-inflamabilidad mediante un ensayo con aceite o líquido de frenos. No obstante, las composiciones actuales ensayadas en el arte, que incluyeran contenidos de cloro disponible y humedad no eran conocidas y especificadas, y ninguna de las composiciones se ensayó de acuerdo con el protocolo de ensayo a la llama de la División 5.1, y se dispone de pocos datos para sustentar estas reivindicaciones.

La idea de encapsular o recubrir hipoclorito de calcio activo con una sal inorgánica hidrosoluble inerte en estas referencias del arte previo era reducir el contacto del hipoclorito de calcio y un material inflamable y, por consiguiente, disminuir su reactividad e inflamabilidad. Las partículas con un recubrimiento de una sal inorgánica como la capa exterior tienen un mayor grado de resistencia a la ignición por cigarrillos encendidos, o a la reacción causada cuando se contactan con materiales orgánicos. Sin embargo, los ensayos de ignición son completamente diferentes en principio del ensayo de clasificación de oxidantes ya mencionado y del sistema de clasificación de la NFPA, que evalúan el aumento en la velocidad de combustión de materiales combustibles luego de que ya se ha iniciado la ignición. El primero es un ensayo de prevención de la ignición del material cuando se contacta con un fósforo encendido, mientras que el ensayo de clasificación de los oxidantes de las Naciones Unidas es para determinar el potencial de aumentar la velocidad de combustión o la intensidad de

combustión de la celulosa combustible cuando los dos se mezclan concienzudamente en una relación específica, en masa, del producto con respecto a la celulosa. Puesto que poco o ningún combustible está presente en los ensayos de ignición, el procedimiento no ensaya la propiedades oxidantes o la capacidad de aumentar la velocidad de combustión de materiales combustibles. Muchas sustancias pasarán los ensayos de ignición, pero se clasificarán aún como oxidantes incluidos en la División 5.1.

Uno de los ejemplos, como se describe en la Patente de los Estados Unidos No. 4,201,756, fue que el hipoclorito de calcio encapsulado, con alrededor de 21% de cloruro de sodio en peso total de la composición, impedía la ignición del material cuando se ponía en contacto con un fósforo encendido, pero no experimentaba descomposición auto-sostenida. En contraste, la mezcla de hipoclorito de calcio y cloruro de sodio en la misma composición en peso acelera efectivamente la combustión, como se indica en la Patente de los Estados Unidos No. 6,638,446.

En consecuencia, es difícil predecir si cualesquiera composiciones en el arte previo pueden clasificarse como un oxidante no incluido en la División 5.1 o como oxidantes Clase 1 o 2 de la NFPA. De hecho, no se ve en el mercado o en la literatura un hipoclorito de calcio granular recubierto, no incluido en la División 5.1, Clase 1 de la NFPA o Clase 2 de la NFPA.

Por lo tanto, existe una creciente necesidad en este arte de fabricar un producto de hipoclorito de calcio con alto cloro disponible, que no se clasifique como oxidante incluido en la División 5.1 o oxidante Clase 3 de la NFPA y que posea una mayor seguridad (es decir, menores propiedades de producir fuego). En consecuencia, esta invención, al ofrecer una solución a esa necesidad, consiste en describir específicamente composiciones de hipoclorito de calcio recubiertas con alto cloro disponible que no sean un oxidante incluido en la División 5.1 o un oxidante Clase 3 de la NFPA, que muestren excelente estabilidad al almacenamiento y que posean ventajas adicionales para tratamientos de agua. Estas composiciones de hipoclorito de calcio recubiertas no se consideran como mercancías peligrosas para

transporte y almacenamiento y, en consecuencia, ofrecerán una mayor seguridad pública.

Adicionalmente, la composición de hipoclorito de calcio recubierta de la presente invención puede proveer una composición, que no es un oxidante no incluido en la División 5.1 o un oxidante Clase 3 de la NFPA, pero que tiene un mayor cloro disponible, menor reactividad y beneficios multi-funcionales que sus mezclas correspondientes para tratamientos de agua y aplicaciones de limpieza.

BREVE SUMARIO DE LA INVENCIÓN

En un aspecto, la presente invención se dirige a una composición para tratamiento de agua, que contiene: hipoclorito de calcio recubierto con un recubrimiento que incluye por lo menos una sal anhidra o hidratada; en donde la composición contiene alrededor de 20% en peso a alrededor de 80% en peso de cloro disponible, basado en el peso total de la composición, y en donde la composición contiene desde alrededor de 1% en peso a alrededor de 50% en peso de agua hidratada, basado en el peso total de la composición, y en donde el recubrimiento incluye desde alrededor de 1% a alrededor de 80% en peso del peso total de la composición, y en donde la composición se clasifica como un oxidante no incluido en la División 5.1 o como un oxidante Clase 1 de la NFPA o Clase 2 de la NFPA.

En otro aspecto, la presente invención se dirige a una composición para tratamiento de agua, que contiene: (a) una capa núcleo interior que incluye hipoclorito de calcio; (b) una o más capas intermedias situadas encima de la capa núcleo interior, incluyendo la capa intermedia una o más sales inorgánicas anhidras o hidratadas, sales orgánicas anhidras o hidratadas, sales poliméricas anhidras o hidratadas, hidróxidos de metal alcalino, hidróxidos de metal alcalinotérreo y sus combinaciones, incluyendo la capa intermedia desde alrededor de 1% a alrededor de 80% en peso del peso total de la composición; y (c) una o más capas exteriores situadas encima de la capa(s) intermedia(s), incluyendo las capas exteriores

por lo menos una sal anhidra o hidratada, incluyendo la capa exterior desde alrededor de 1% a alrededor de 35% en peso del peso total de la composición; en donde la composición contiene alrededor de 20% en peso a alrededor de 80% en peso de cloro disponible, basado en el peso total de la composición; en donde la composición contiene desde alrededor de 1% en peso a alrededor de 50% en peso de agua hidratada, basado en el peso total de la composición; y en donde la composición se clasifica como un oxidante no incluido en la División 5.1 o como un oxidante Clase 1 de la NFPA o un oxidante Clase 2 de la NFPA.

Éstos y otros aspectos de la invención se harán evidentes luego de leer la siguiente descripción detallada de la invención.

BREVE DESCRIPCIÓN DE LOS DIBUJOS

La invención se entenderá si se toma en conjunción con los siguientes dibujos, en los cuales:

Figura 1 es un dibujo esquemático de un hipoclorito de calcio recubierto, multi-capa, incorporado por la presente invención;

Figura 2 es un análisis de mapa elemental de la muestra 3 de la presente invención;

Figura 3 es una imagen de una muestra recubierta 16 de la presente invención; y

Figura 4 es un análisis de mapa elemental de la muestra recubierta 16 de la presente invención.

DESCRIPCIÓN DETALLADA DE LA INVENCIÓN

Esta invención provee una composición de hipoclorito de calcio granular recubierta, mejorada para baja reactividad durante la manipulación, almacenamiento y transporte y tratamiento de microorganismos en piscinas, balnearios (*"spas"*), agua y otras aplicaciones hídricas industriales y recreativas. La composición de hipoclorito de calcio recubierta de la

invención se recubre con suficientes cantidades de una o más sales hidratadas para proporcionar un oxidante estable, no incluido en la División 5.1. Las sales inorgánicas hidratadas preferidas son sales de metal alcalino y alcalinotérreo de haluro, sulfato, fosfato, silicato, borato, que son relativamente estables durante por lo menos un día a alrededor de 45°C contra su deshidratación. Las sales poliméricas y orgánicas preferidas son aquellas sales de metal alcalino de ácido orgánico y ácido polimérico, y sus hidratos relativamente estables.

Un aspecto de esta invención es una composición de hipoclorito de calcio recubierta, multi-capa, que incluye un núcleo de hipoclorito de calcio granular, recubierto con una o más sales hidratadas. Esta composición recubierta multi-capa incluye 1) una capa núcleo interior que contiene hipoclorito de calcio anhidro o hidratado; o una mezcla de los mismos; 2) una o más capas exteriores que contienen una o más sales hidratadas o una mezcla de las mismas; y 3) una o más capas intermedias que contienen un hidróxido de metal alcalino o alcalinotérreo, una sal inorgánica, una sal orgánica o una sal polimérica, incluidas formas anhidras e hidratadas de tales sales, o una mezcla de las mismas. Estos recubrimientos de sales evitan la interacción química del hipoclorito de calcio con los materiales de recubrimiento de sales hidratadas en la capa exterior y, por lo tanto, impiden la degradación del hipoclorito de calcio.

Otro aspecto de esta invención es producir una composición de un oxidante no incluido en la División 5.1, recubierta, con alto cloro disponible, excelente estabilidad al almacenamiento y aplicaciones multi-funcionales para agua y otros tratamientos. La composición de hipoclorito de calcio recubierta no se considera como mercancía peligrosa para transporte y almacenamiento, y brindará una mayor seguridad pública.

Un aspecto adicional de esta invención es producir una composición de hipoclorito de calcio recubierta en donde o bien las capas exteriores o bien las capas interiores de la composición multi-capa o de la composición recubierta mono-capa (***"the single layer coated composition "***) contienen un purificador, inhibidor de costra de óxido, dispersante, suavizante de

agua, inhibidor de la corrosión, alguicida, fungicida o aglutinante, para obtener las propiedades deseadas de homogeneidad, liberación controlada y efectos multi-funcionales en agua y otras áreas de tratamiento.

La composición preferida de hipoclorito de calcio recubierta multi-capa puede emplear sales hidratadas o anhidras específicas para obtener un contenido de agua hidratada total y cloro disponible para reducir su reactividad y velocidad de combustión frente a un material activo tal como glicol, celulosa, aceite, líquido de frenos y materiales poliméricos.

Las composiciones de hipoclorito de calcio recubiertas de esta invención contienen preferiblemente alrededor de 20 a alrededor de 80% de cloro disponible y alrededor de 1 a alrededor de 80% de materiales de recubrimiento, y alrededor de 1 a alrededor de 50% de agua hidratada, en peso total de la composición recubierta.

Adicionalmente, la composición de hipoclorito de calcio recubierta de la presente invención puede proporcionar una composición homogénea que no es un oxidante no incluido en la División 5.1, pero que tiene un cloro disponible y beneficios multi-funcionales mayores que sus correspondientes mezclas para tratamiento de agua y otras aplicaciones.

El término "sal hidratada", tal como se emplea en las presentes especificación y reivindicaciones, se define como cualquier sal inorgánica hidratada, sal orgánica, sal polimérica y base inorgánica, o una mezcla de las mismas. El término "hidratado", tal como se emplea en este contexto, tiene como fin incluir cualquiera de tales sales o bases, que contienen una o más aguas de hidratación, incluidas mezclas de aguas de hidratación.

El término "hidratado", tal como se emplea en conjunción con hipoclorito de calcio en las presentes especificación y reivindicaciones, se refiere a hipoclorito de calcio que tiene un contenido de agua de por lo menos 5% en peso del hipoclorito de calcio. Preferiblemente, estas composiciones son hipoclorito de calcio comercial "hidratado" (5.5% a 16% de agua), número CAS 7778-54-3.

El término "anhidro", tal como se emplea en las presentes especificación y reivindicaciones en conjunción con sales, tiene como

finalidad ser cualquier sal inorgánica no hidratada, sal inorgánica, sal orgánica, sal polimérica o base inorgánica, o una mezcla de las mismas. El mismo término, cuando se emplea en conjunción con hipoclorito de calcio, se refiere a hipoclorito de calcio que tiene un contenido de agua de menos de 5% en peso del hipoclorito de calcio.

De acuerdo con la presente invención, las partículas de hipoclorito de calcio recubiertas con una sal anhidra o hidratada como la capa exterior tendrán un mayor grado de resistencia a la ignición por cigarrillos prendidos para reducir la velocidad de combustión causada por hipoclorito de calcio, y para minimizar la reacción causada cuando se pone en contacto con materiales orgánicos.

Además, de acuerdo con la presente invención, se proveen composiciones de hipoclorito de calcio granular recubiertas tanto mono-capa como multi-capa, que pueden clasificarse como oxidante no incluido en la División 5.1, en donde el término "composición de oxidante no incluido en la División 5.1", tal como se emplea en las presentes especificación y reivindicaciones, se refiere a cualesquiera composiciones recubiertas de gránulos de hipoclorito de calcio con una sal inorgánica anhidra o hidratada, sal orgánica, sal polimérica, una base, o su(s) hidrato(s), y una mezcla de los mismos, que no se clasifica como oxidante incluido en la División 5.1 de las Naciones Unidas, de acuerdo con procedimientos de ensayos estándar actualmente vigentes. Alternativamente, las composiciones de la presente invención pueden clasificarse o bien como oxidantes Clase 1 de la NFPA o Clase 2 de la NFPA.

Adicionalmente, el ensayo de clasificación actual de oxidantes de las Naciones Unidas puede llevarse igualmente a cabo para determinar el potencial de un producto de hipoclorito de calcio para aumento en la velocidad de combustión o la intensidad de combustión de la celulosa combustible cuando los dos se mezclan concienzudamente en ambas relaciones 1:1 y 4:1, en masa, del producto con respecto a la celulosa. Más aún, ensayos de combustión pueden realizarse asimismo con el producto en

contacto con materiales combustibles, tales como cubos y bolsas que pueden emplearse como embalaje, para determinar el potencial de un producto de hipoclorito de calcio para aumentar la velocidad de combustión de los materiales combustibles.

Comúnmente se reconoce que entre más elevado el contenido de humedad de la composición de hipoclorito de calcio, menos estable es el hipoclorito de calcio. Por lo tanto, debe considerarse un contenido de humedad hidratada balanceado y apropiado de un material de recubrimiento para proveer una composición de hipoclorito de calcio recubierta, relativamente estable, con alto cloro disponible.

Los materiales de recubrimiento en la presente invención incluyen sales inorgánicas anhidras e hidratadas "hidrosolubles" e "inertes", sales orgánicas, sales poliméricas, e "ingredientes activos" opcionales, en donde el término "inerte", definido como poca reactividad química al hipoclorito de calcio, que causa una degradación seria y una mayor reactividad, y preferiblemente el término "hidrato" se refiere a cualquier sal hidratada que contiene más del 20% de contenido de agua hidratada. El término "hidrosoluble" se emplea como solubilidad de una sal en agua desde alrededor de 5 a alrededor de 100%. El término "ingredientes activos" se refiere a químicos conocidos para el tratamiento de agua, que son compatibles con hipoclorito de calcio. Además, el término "hidratos" en la presente invención incluye una mezcla de hidratos de sales inorgánicas, sales orgánicas, sales poliméricas, e hidróxidos de metal alcalino y alcalinotérreo, y una mezcla de los mismos.

Las composiciones de esta invención incluyen preferiblemente gránulos recubiertos de hipoclorito de calcio que contienen uno o más recubrimientos de una sal hidratada o anhidra. Típicamente, los gránulos de hipoclorito de calcio en la capa núcleo interior de la presente invención tienen alrededor de 54 a alrededor de 80% de cloro disponible y alrededor de 0% a alrededor de 12% de contenido de humedad con tamaños de partícula que varían desde alrededor de 50 a alrededor de 4.000 micrones de diámetro. Los granos de hipoclorito de calcio típicos en la capa núcleo

interior contienen hipoclorito de calcio hidratado, anhidro, o una mezcla de los mismos.

La composición de hipoclorito de calcio recubierta mono-capa de la presente invención comprende una capa de recubrimiento única que contiene una o más sales hidratadas o formas anhidras de las sales, así como cualesquiera ingredientes opcionales enumerados en esta solicitud.

Ejemplos típicos en la presente invención incluyen sales que son conocidas por formar agua hidratada elevada con más 20% de contenido de agua hidratada, tales como sulfato de sodio, metaborato de litio, carbonato de sodio, ortofosfato de sodio, ortofosfato monohidrogenado de sodio, fosfato de sodio, pirofosfato de sodio, tetraborato de sodio, silicato de sodio, sulfato de aluminio, metasilicato de sodio, sulfato de aluminio y sodio, sulfato de magnesio, sulfato de potasio y aluminio, sulfato de zinc, sulfato de cobre, y citrato de sodio y sal de sodio de ácido poli(acrílico – ácido maleico). Estas sales son las que con mayor frecuencia forman sal hidratada con alto contenido de agua hidratada (aguas de hidratación), cuando su solución acuosa se seca por aspersión bajo las condiciones de recubrimiento.

De acuerdo con una incorporación preferida de la presente invención, el material de recubrimiento puede contener opcionalmente un ingrediente activo adicional para piscinas, balnearios y tratamiento de agua, tales como purificadores de agua, inhibidores de costra de óxido, suavizantes de agua, inhibidores de la corrosión, alguicidas, fungicidas, aglutinantes, o una mezcla de los mismos. Tales ingredientes, así como otros, son conocidos por los expertos en el arte. Particularmente, el ingrediente activo adicional en la presente invención incluye componentes de ingrediente activo que tienen propiedades funcionales conocidas, tales como sulfato de cobre, sulfato de zinc, sulfato de aluminio, citrato de sodio, borato de sodio, tripolifosfato de sodio (STPP), hexametafosfato de sodio (SHMP), 1,3-dicloro-5,5-dimetilhidantoína (DCDMH), 1,3-dibromo-5,5dimetilhidantoína (DBDMH), 1-bromo-3-cloro-5,5-dimetilhidantoína (BCDMH), 1,3-dicloro-5-etil-5-metilhidantoína (DCEMH), 1,3-dibromo-5-etil-5-metilhidantoína

(DBEMH), 1-bromo-3-cloro-5-metil-5-etilhidantoína (BCEMH), tricloro-, dicloro- y monoclorotriazina, bicloruro de dicloro-s-triazinatriona de sodio, su forma hidratada, y una mezcla de los mismos. Cantidades de estos ingredientes activos adicionales varían preferiblemente desde alrededor de 0.1 a alrededor de 5% en peso, basado en el peso total de la composición recubierta.

El contenido total del material de recubrimiento en la composición de hipoclorito de calcio recubierta preferida en la presente invención es desde alrededor de 1 a alrededor de 80% en peso, y el cloro total disponible del hipoclorito de calcio granular es desde alrededor de 20 a alrededor de 80%, basado en el peso total de las composiciones de hipoclorito de calcio recubiertas. El contenido de humedad total del hipoclorito de calcio granular recubierto es alrededor de 1% a alrededor de 50%, basado en el peso total de la composición de hipoclorito de calcio recubierta. El contenido preferido de agua hidratada en el material de recubrimiento es mayor de 15%, preferiblemente, mayor de 20% en peso total de los materiales de recubrimiento.

La composición de hipoclorito de calcio recubierta multi-capa en la presente invención puede incluir por lo menos tres capas, como se muestra en Figura 1: 1) una capa núcleo interior que contiene gránulos de hipoclorito de calcio anhidro o hidratado; 2) una capa intermedia que contiene una sal inorgánica anhidra, sal orgánica, sal polimérica, o una base de metal alcalino o alcalinotérreo, o su(s) hidrato(s) estable(s), o una mezcla de los mismos, como una capa protectora contra la interacción interfacial de hipoclorito de calcio y los materiales de recubrimiento en las capas exteriores; 3) una capa exterior que contiene un hidrato anhidro hidrosoluble y una sal inorgánica hidratada, sal orgánica o sal polimérica, químicos activos para tratamiento de agua, o una mezcla de los mismos.

El material de recubrimiento en las capas exteriores de la presente invención contiene por lo menos una sal hidratada o anhidra, como ya se describió, para los materiales de recubrimiento en el hipoclorito de calcio recubierto mono-capa. El hidrato preferido de sal es un hidrato con un alto

porcentaje de agua hidratada cuando se disuelve en agua, y luego se seca bajo las condiciones de recubrimiento.

Más preferiblemente, de acuerdo con la presente invención, la sal hidratada preferida en la capa exterior es una que tiene una baja conductividad térmica y genera los máximos contenidos de agua hidratada en peso de material de recubrimiento luego del recubrimiento, y deshidrata la totalidad o la mayor parte del agua hidratada por debajo de alrededor de 200°C. Estas sales son las que más tienden a producir un hipoclorito de calcio recubierto, multi-capa, no incluido en la División 5.1, con el cloro disponible más alto posible.

Muchas sales inorgánicas y sus hidratos son conocidos y son obtenibles y se seleccionan para elaborar una solución de recubrimiento para recubrir hipoclorito de calcio granular en la presente invención. Ejemplos típicos en la presente invención incluyen sales que son conocidas para formar agua hidratada elevada, descritas como materiales de recubrimiento para el hipoclorito de calcio recubierto mono-capa.

Puede emplearse cualquier combinación de sales anhidras o hidratadas para elaborar una solución acuosa para el recubrimiento de la capa exterior. Se elabora igualmente una sal hidratada *in situ* del óxido correspondiente con el ácido correspondiente como la solución de recubrimiento. Por ejemplo, 20% de una solución de sulfato de magnesio acuosa puede prepararse de óxido de magnesio y ácido sulfúrico en una relación molar de alrededor de 1:1 en la cantidad apropiada de agua a temperatura de la sala.

La concentración de una sal en la solución de recubrimiento puede variar dependiendo de su solubilidad y viscosidad para el proceso de recubrimiento, y el contenido en los materiales de recubrimiento, y preferiblemente se aplica una concentración elevada por consideraciones de costos. Las elecciones de sales particulares son conocidas por los expertos en el arte.

En la incorporación más preferida de esta invención, las sales inorgánicas y sus hidratos empleados para generar una solución acuosa para

las capas exteriores incluyen sulfato de magnesio, fosfato de sodio, pirofosfato de sodio, sulfato de cobre, un hidrato de estas sales, o una mezcla de los mismos. Una solución acuosa de tal sal o su hidrato produce el hidrato sólido o una mezcla de los hidratos luego del recubrimiento dependiendo de las condiciones de recubrimiento.

Por ejemplo, cuando la solución se prepara de sulfato de magnesio, formas hidratadas de sulfato de magnesio, tales como heptahidrato de sulfato de magnesio, o de óxido de magnesio y ácido sulfúrico, hidratos de sulfato de magnesio con número de hidratación de 3 a 7 bajo diferentes condiciones de recubrimiento, la composición de hipoclorito de calcio granular recubierta con tetrahidrato de sulfato de magnesio con un número hidratado promedio de 3-4 proporciona una mejor estabilidad al almacenamiento que sus formas hidratadas más altas.

Las capas exteriores de la composición de hipoclorito de calcio recubierta de acuerdo con la presente invención incluyen asimismo una sal orgánica de metal alcalino o alcalinotérreo hidratada y/o anhidra, o sales poliméricas. Ejemplos de sales orgánicas y poliméricas incluyen una sal de sodio de ácido cítrico, ácido benzoico, ácido oxálico, ácido poliacrílico, ácido polimaleico, ácido poli(acrílico-ácido co-maleico), ácido policpoxisuccínico, y sus hidratos estables. Generalmente la sal polimérica es una parte de los materiales de recubrimiento con una sal inorgánica hidratada y/o anhidra. El contenido de la sal polimérica es de alrededor de 0.5 a alrededor de 15% en peso de todos los materiales de recubrimiento.

En una incorporación preferida de la presente invención, el contenido total del material de recubrimiento en las capas exteriores es desde alrededor de 1 a alrededor de 35% en peso total de la composición de hipoclorito de calcio recubierta. El contenido total de la humedad de los materiales de recubrimiento en las capas exteriores en la presente invención es superior a 15%, preferiblemente, superior a 20% en peso de los materiales de recubrimiento.

Las capas exteriores del hipoclorito de calcio recubierto en la presente invención pueden incluir un ingrediente activo tal como un

purificador, inhibidor de costra de óxido, suavizante de agua, inhibidor de la corrosión, alguicida, fungicida o aglutinante, o una mezcla de los mismos. Los ejemplos preferidos son aquellos ingredientes activos descritos como un ingrediente activo en el hipoclorito de calcio granular recubierto mono-capa. Cantidades de estos ingredientes activos adicionales varían preferiblemente desde alrededor de 0.1 a alrededor de 5% en peso, basado en el peso total de la composición recubierta.

La composición de la capa intermedia en la presente invención contiene una sal inorgánica hidratada y/o anhidra, una sal orgánica y una sal polimérica o un hidróxido de metal alcalino o alcalinotérreo, o una mezcla de los mismos. El hidróxido de metal alcalino y alcalinotérreo y la sal anhidra y su hidrato en la capa intermedia descrita en la presente invención se emplean como capa protectora de la interacción superficie-superficie de hipoclorito de calcio, y los hidratos y otros ingredientes en las capas exteriores contra la pérdida de cloro durante el almacenamiento y el transporte.

De acuerdo con la presente invención, típicamente la capa intermedia contiene cloruros de metal alcalino, anhidros y/o menos hidratados, sulfatos, fosfatos, silicatos o boratos, y un hidróxido de metal alcalino y alcalinotérreo. La sal y la base preferidas son cloruro de calcio, sulfato de sodio, borato de sodio, silicato de sodio, hidróxido de litio e hidróxido de calcio. Los componentes de la capa intermedia pueden ser asimismo ingredientes activos.

El hipoclorito de calcio se descompone rápidamente en la presencia de un ácido y es más estable por encima de pH 9. En consecuencia, se prefiere mantener las composiciones en la capa intermedia lejos de los rangos de pH ácido. El uso de un hidróxido de metal en la capa intermedia tiene por finalidad estabilizar el hipoclorito de calcio contra su descomposición, manteniendo el pH básico del hipoclorito de calcio recubierto, y absorber el cloro generado durante el almacenamiento. El hidróxido de metal preferido es hidróxido de calcio.

El contenido de los materiales de recubrimiento en la capa intermedia es alrededor de 1 a alrededor de 80%, preferiblemente, alrededor de 3 a alrededor de 75%, basado en el peso total de la composición de hipoclorito de calcio recubierta. El cloro total disponible del hipoclorito de calcio recubierto multi-capa es desde alrededor de 20 a alrededor de 80%, y el contenido de humedad total es alrededor de 1 a alrededor de 50% en peso total del hipoclorito de calcio recubierto. El espesor de las partículas de hipoclorito de calcio recubierto mono-capa y multi-capa se controla por el tamaño de partícula del hipoclorito de calcio y la cantidad de los materiales de recubrimiento utilizados para los recubrimientos. Típicamente, de acuerdo con la presente invención, el espesor del recubrimiento está entre 10-200 μm.

De acuerdo con la presente invención, se emplean SEM y técnicas de mapa elemental para caracterizar la forma y la uniformidad de la capa del recubrimiento; se emplea EDS para determinar el espesor del recubrimiento y se usa XRD para determinar la forma de hidrato del hipoclorito de calcio y la sal.

La cantidad de humedad en el hipoclorito de calcio recubierto puede determinarse por cualquier método analítico estándar para medir agua en hipoclorito de calcio y composiciones de hipoclorito de calcio recubiertas. El método preferido es análisis termo-gravimétrico (TGA). Se reveló igualmente la forma de hidrato del material de recubrimiento, basándose en el peso de la humedad aportada al material de recubrimiento sobre el peso del material de recubrimiento empleado.

El cloro disponible del hipoclorito de calcio recubierto se determina por un método analítico estándar, empleado para ensayo de un hipoclorito de calcio típico, a menos que el método se vea interferido por un material de recubrimiento.

La composición de hipoclorito de calcio granular recubierta en la presente invención consta de alrededor de 1 a alrededor de 50%, preferiblemente, alrededor de 4 a alrededor de 30% del contenido de humedad hidratada, y alrededor de 20 a alrededor de 80%, preferiblemente

alrededor de 30% a alrededor de 60% de cloro disponible en peso de los gránulos de hipoclorito de calcio recubiertos. Los tamaños de partícula de los gránulos recubiertos están en el rango desde alrededor de 40 a alrededor de 5.000 μm, preferiblemente alrededor de 200 a alrededor de 5.000 μm de diámetro.

Basado en la presente invención, el hipoclorito de calcio granular recubierto ofrece muchas ventajas sobre la mezcla correspondiente. Por ejemplo, cuando el hipoclorito de calcio granular, que contiene 68% de cloro disponible con el tamaño de partícula de alrededor de 200 a alrededor de 2.000 micrones, se aplica para recubrimiento con hidratos de sulfato de magnesio, la composición de hipoclorito de calcio recubierta resultante contiene alrededor de 56% de cloro disponible, alrededor de 18% de sulfato de magnesio hidratado y menos de 14% de humedad hidratada en peso de los gránulos totales de hipoclorito de calcio recubiertos. No obstante, cuando se emplea hipoclorito de calcio para mezclar con heptahidrato de sulfato de magnesio, la mezcla de hipoclorito de calcio contiene únicamente alrededor de 47% de cloro disponible, alrededor de 30% heptahidrato de sulfato de magnesio y alrededor de hasta 20.4% de humedad hidratada en peso total de la mezcla.

Lo que es muy importante, la composición de hipoclorito de calcio específicamente recubierta en la presente invención no sólo contiene cloro disponible más alto, sino que provee además una excelente estabilidad a temperaturas elevadas, que su mezcla correspondiente.

Por ejemplo, la composición de hipoclorito de calcio granular recubierta, que contiene alrededor de 54% de cloro disponible, alrededor de 21% de hidratos de sulfato de magnesio, donde la mayoría de los hidratos son tetrahidrato de sulfato de magnesio, y alrededor de 10% de humedad hidratada en peso total de la composición, se clasifica como un oxidante no incluido en la División 5.1 con excelente estabilidad en horno durante 10, 20 y 30 días a 45°C. No obstante, el cloro disponible máximo de la mezcla de hipoclorito de calcio con heptahidrato de sulfato de magnesio es únicamente de alrededor de 47.8% de cloro disponible, y la estabilidad en

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horno de la mezcla a 45°C no fue tan buena como la composición recubierta.

Adicionalmente, la composición de hipoclorito de calcio granular recubierta, que contiene alrededor de 47% de cloro disponible, alrededor de 29% de tetrahidrato de sulfato de magnesio y alrededor de 10% de humedad hidratada, con hipoclorito de calcio anhidro en la capa núcleo interior [difiere] del hipoclorito de calcio que contiene 68% de cloro disponible muestra la estabilidad excelente con poca pérdida de cloro disponible durante 30 días a una temperatura entre 45 y 50°C.

Análogamente, la excelente estabilidad con poca pérdida de cloro disponible se observó durante 30 días a una temperatura entre 45 y 50°C para la composición de hipoclorito de calcio granular recubierta, en donde la muestra consta de alrededor de 56% de cloro disponible, alrededor de 28% de tetrahidrato de sulfato de magnesio, y alrededor de 10% de humedad hidratada con hipoclorito de calcio anhidro en la capa núcleo interior del hipoclorito de calcio con 78% de cloro disponible. El hipoclorito de calcio granular recubierto es mucho más estable que el no recubierto y sus mezclas con heptahidrato de sulfato de magnesio.

Adicionalmente, el hipoclorito de calcio granular recubierto en la presente invención ofrece otra ventaja sobre la mezcla correspondiente. Por ejemplo, cuando el hipoclorito de calcio granular, que contiene 68% de cloro disponible con el tamaño de partícula de alrededor de 200 a alrededor de 2.000 micrones, se recubre con hidratos de sulfato de magnesio, la composición de hipoclorito de calcio recubierta resultante con alrededor de 52% de cloro disponible y alrededor de 9.5% de humedad hidratada en peso de los gránulos de hipoclorito de calcio recubiertos totales se clasifica como un oxidante no incluido en la División 5.1 y un oxidante NAFP-1. No obstante, cuando la mezcla del hipoclorito de calcio con hidratos de sulfato de magnesio contiene los mismos cloro disponible y humedad no es un oxidante no incluido en la División 5.1 y NFPA-1.

Típicamente, en la presente invención, una composición de hipoclorito de calcio recubierta se produce por un equipo de recubrimiento

de lecho fluidizado con aspersión tal como el Mini-Glatt y GPCG-1 de Glatt Air Technologies, Inc., y el ACT 100N y el ACT 300N de Applied Chemical Technology, Inc. Las variables y condiciones de recubrimiento se controlan específicamente para que tengan una humectación mínima en la superficie de las partículas de hipoclorito de calcio, y generen mezclas apropiadas con sales hidratadas. Un recubrimiento multi-capa se obtiene mediante alimentación secuencial de materiales de recubrimiento apropiados bajo condiciones de recubrimiento adecuadas. El recubrimiento puede conducirse utilizando o bien un proceso por lotes o bien un proceso continuo. Adicionalmente, de acuerdo con la presente invención, se emplea una alimentación continua de solución de recubrimiento acuosa para producir una composición de hipoclorito de calcio granular recubierta mono-capa o multi-capa controlada.

Los múltiples factores e la composición de hipoclorito de calcio recubierta, tales como cloro disponible, forma hidratada, tipo y conductividad térmica de los materiales de recubrimiento, estabilidad de los hidratos frente a su deshidratación, contenido de humedad hidratada total, capas de recubrimiento consecutivas, son importantes para reducir su reactividad y velocidad de combustión frente a un material activo tal como glicol, celulosa, aceite o fluido para frenos y materiales poliméricos, y mejoran su estabilidad al almacenamiento y desempeño para tratamientos de agua y otros tratamientos.

Las composiciones de hipoclorito de calcio granular recubiertas de la presente invención son fáciles de empacar, almacenar, despachar para uso en los tratamientos de agua y similares. Específicamente, los gránulos recubiertos son útiles como desinfectantes en tratamientos de agua (por ejemplo, en piscinas de natación y balnearios), tratamientos de aguas industriales y similares y, específicamente, son más seguros de transportar y almacenar que el hipoclorito de calcio mismo.

De acuerdo con la presente invención, la composición de hipoclorito de calcio recubierta se mezcla en una relación apropiada con otros aditivos, incluidos hidratos de sal inorgánica, sal orgánica y sal polimérica, y un

purificador, inhibidor de costra de óxido, floculantes, inhibidor de la corrosión, alguicida, fungicida y otros aditivos para piscinas, balnearios y aditivos para tratamientos de agua.

Finalmente, de acuerdo con la presente invención cualquier configuración y formas de hipoclorito de calcio, incluidas tabletas, aglomerados, briquetas, redondas, irregulares y en cualquier tamaño, pueden recubrirse con los materiales de recubrimiento descritos anteriormente, y ofrecen beneficios similares sobre las mezclas correspondientes.

De acuerdo con la presente invención, la tecnología de recubrimiento es apropiada para recubrir otros ingredientes activos para piscinas, balnearios y tratamiento de agua por su baja reactividad y mejor estabilidad durante la manipulación, almacenamiento y transporte, y para el control de microorganismos.

Los siguientes ejemplos tienen como finalidad ilustrar aún más, pero de ningún modo limitar, el ámbito de la presente invención. Todas las partes y porcentajes son en peso y todas las temperaturas son grados Celsius, a menos que explícitamente se manifieste lo contrario.

EJEMPLOS

Los siguientes ejemplos citados en la presente invención describen y demuestran con más detalle las incorporaciones preferidas dentro del ámbito de la presente invención. Los ejemplos se incluyen únicamente con fines de ilustración y no tienen que entenderse como limitaciones de la presente invención, puesto que muchas variaciones de la misma son posibles dentro del ámbito.

Procedimientos Generales

Los análisis de humedad y cloro disponible se llevaron a cabo utilizando los métodos estándar empleados para análisis del hipoclorito de calcio no recubierto. Se empleó el método del ensayo a la llama para sustancias oxidantes, descrito en la Sección 34 del Protocolo de las

Naciones Unidas, para determinar las características de los diferentes productos de hipoclorito de calcio recubiertos, descritos a continuación. El método de ensayo detallado se describe en las Recomendaciones de las Naciones Unidas para el Transporte de Mercancías Peligrosas; Manual de Ensayos y Criterios; Tercera Edición Revisada; Sección 34 "Procedimientos de Clasificación, Métodos de Ensayo y Criterios Relativos a Sustancias Oxidantes de la División 5.1.

Para clasificación, un oxidante no incluido en la División 5.1 es una sustancia que, en las dos relaciones 4:1 y 1:1 de la muestra a celulosa (en masa) ensayadas, no prende fuego y se incendia, o exhibe tiempos medios de combustión superiores a los de una mezcla 3:7 (en masa) de bromato de potasio y celulosa, donde el tiempo de combustión se toma desde cuando se prende la energía eléctrica hasta cuando termina la reacción principal (por ejemplo, llama, incandescencia o combustión incandescente).

Una prueba de combustión a escala mediana de hipoclorito de calcio formulado granular, empacado, sal empacada y empaque vacío se utilizó para medir y comparar la velocidad de convección de la liberación de calor, flujo de calor de irradiación, pérdida de masa del producto granular empacado, sal empacada y empaque vacío cuando se expusieron a un fuego de propano de 46 kW. El resultado se emplea para determinar la contribución del oxidante granular a la velocidad de combustión de materiales de empaque combustibles típicos.

El hipoclorito de calcio recubierto en los siguientes ejemplos se produce típicamente por un equipo de recubrimiento de lecho fluidizado con aspersión, tal como Mini-Glatt y GPCG-1 de Glatt Air Technologies, Inc., y ACT 100N y ACT 300N de Applied Chemical Technology, Inc., con una temperatura del aire de entrada de 50-75°C y temperaturas del producto de 35-55°C. Se efectuó un recubrimiento multi-capa mediante alimentación secuencial de materiales de recubrimiento bajo las condiciones con las mismas o diferentes temperaturas de entrada y producto. La velocidad de bombeo de una solución de recubrimiento se controló específicamente para obtener una humectación y secamiento apropiados de partícula con el fin de

minimizar la pérdida de cloro disponible. Como se sabe en el arte, aunque estos ejemplos se realizaron usando un proceso en lotes, para la producción de estos materiales pueden emplearse igualmente otros procesos, tales como procesos continuos.

EJEMPLO 1: Composiciones de Hipoclorito de Calcio Recubiertas y Clasificación.

Tabla 1 presenta las composiciones de hipoclorito de calcio recubiertas de los ejemplos 1-10, incluidos el tipo de hipoclorito de calcio, cloro disponible y composición, material de recubrimiento y humedad, y clasificación en la División 5.1. La composición del hipoclorito de calcio no recubierto inicial contenía alrededor de 68% de cloro disponible, alrededor de 6.6% de humedad con un tamaño de partícula típico en el rango de 200-2.000 µm de diámetro. En Tabla 1, las muestras 1 a 9 incluyen hipoclorito de calcio: 68% de cloro disponible, tamaño de partícula: ~200-2.000 µm con ~6.6% de humedad; la muestra 10 incluye hipoclorito de calcio: 78% cloro disponible, tamaño de partícula: ~100-2.000 µm con ~10.2% de humedad, se empleó para recubrimiento (sic). Los porcentajes de ingredientes se refieren a porcentajes en peso.

Tabla 1 Composición del Hipoclorito de Calcio Granular Recubierto y Clasificación

Muestra #	Composición de Gránulos de Hipoclorito de Calcio Recubiertos				AvCl #* (%)	Humedad (%)	No incluido en División 5.1
	Capa Núcleo	1ª. Capa	2ª. Capa	3ª. Capa			
1	77.3% $Ca(OCl)_2 \cdot xH_2O$	0.7% NaOH	22.0% $MgSO_4 \cdot xH_2O$	-	52.2	17.1	SÍ
2	83.4% $Ca(OCl)_2 \cdot xH_2O$	0.7% NaOH	13.4% $MgSO_4 \cdot xH_2O$	2.5%poli(AM) $Na \cdot nH_2O$*	55.9	13.8	SÍ
3	82.0% $Ca(OCl)_2 \cdot xH_2O$	1.8% NaCl	16.2% $MgSO_4 \cdot xH_2O$	-	55.0	14.0	SÍ
4	81.5% $Ca(OCl)_2 \cdot xH_2O$	1.6% $Ca(0)_2$	16.9% $MgSO_4 \cdot xH_2O$	-	51.3	15.0	SÍ

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5	807% $Ca(OCl)_2 \cdot xH_2O$	-	19.3% $MgSO_4 \cdot xH_2O$	-	54.7	10.9	Sí
6	74.3% $Ca(OCl)_2$ xH_2O	1.5% NaCl	24.2% $MgSO_4 \cdot xH_2O$	-	50.9	8.7	Sí
7	805% $Ca(OCl)_2 \cdot xH_2O$	-	19.5% $MgSO_4 \cdot xH_2O$	-	54.4	9.2	Sí
8	73.6% $Ca(OCl)_2 \cdot xH_2O$	-	26.4% $MgSO_4 \cdot xH_2O$	-	50.8	9.6	Sí
9	69% $Ca(OCl)_2 \cdot xH_2O$	-	31% $MgSO_4 \cdot xH_2O$	-	47.2	10.2	Sí
10	72% $Ca(OCl)_2 \cdot xH_2O$	-	28% $MgSO_4 \cdot xH_2O$	-	56.1	10.4	Sí

* Poli(AM)Na: sal de sodio de ácido poli(acrílico – ácido co-maleico);

** AvCl: cloro disponible

El análisis XRD de las muestras 5 a 8 indica que el hipoclorito de calcio en la capa núcleo interior consta de una mezcla de alrededor de 70% de hipoclorito de calcio anhidro y alrededor de 30% de hipoclorito de calcio hidratado, donde el hipoclorito de calcio no recubierto contiene por lo menos 70% de forma hidratada de hipoclorito de calcio, y la capa núcleo interior de las muestras 9 y 10 contienen casi todas hipoclorito de calcio anhidro. El análisis XRD del hidrato de sulfato de magnesio en la capa exterior mostró que la mayoría es su tetrahidrato. El análisis en húmedo de la humedad de las muestras recubiertas 1 a 4 indica que los hidratos de sulfato de magnesio en la composición contienen un agua hidratada promedio de alrededor de 6.

Como lo indican los datos en la Tabla 2, las muestras recubiertas 6 a 8 muestran una estabilidad en horno similar al hipoclorito de calcio no recubierto a 45°C durante 10, 20 y 30 días, que se consideran simulaciones equivalentes a 1, 2 y 3 años de tiempo de almacenamiento bajo condiciones de almacenamiento ordinarias. Sorprendentemente, las muestras recubiertas

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9 y 10 muestran la excelente estabilidad durante 30 días a 45°C. Se observó poca pérdida del cloro disponible.

Tabla 2. Estabilidad en Horno de Hipoclorito de Calcio Recubierto vs. No Recubierto a 45°C

Muestra	AvCl % luego del día 0	Pérdida AvCl % luego de 10 días	Pérdida AvCl luego de 20 días	Pérdida AvCl luego de 30 días
No cubierta	69.2	2.9	8.7	15.9
5	54.5	4.4	16.3	26.4
6	50.9	3.5	7.0	12.7
7	54.4	4.6	8.6	16.7
8	50.8	-0.18	7.5	11.8
9	47.2	-1.3	-0.09	-1.54
10	56.1	-0.3	1.0	3.3

Tabla 3 presenta la comparación del ejemplo 7 y la mezcla correspondiente, incluido tipo de hipoclorito de calcio, cloro disponible, composición, material de recubrimiento y humedad contra su clasificación División 5.1. La composición del hipoclorito de calcio no recubierto inicial contenía 69% de cloro disponible, alrededor de 9.2% de humedad con un tamaño de partícula medio en el rango de 200-2.000 µm de diámetro.

Tabla 3. Composición del Hipoclorito de Calcio Granular Recubierto y Clasificación (hipoclorito de calcio: ~78% AvCl con tamaño de partícula ~100 a 2.000 µm en muestras 11 y 8)

ID de la Muestra	Material de recubrimiento y su contenido en el producto recubierto		AvCl (%)	Humedad (%)	No incluido en la División 5.1
	Hipoclorito de calcio del núcleo	Capa exterior			
7	80.5%	19.5%$MgSO_4 \cdot xH_2O$	54.4	9.2	SÍ
Mezcla 80/20 del hipoclorito de calcio / $MgSO_4.7H_2O$			54.5	15.3	NO

Tal como se muestra en la Tabla 3, la muestra mezclada con heptahidrato de sulfato de magnesio, que tiene el mismo cloro disponible que la muestra recubierta 7, no es un oxidante no incluido en la División 5.1.

Tabla 4 muestra algunos beneficios de la composición de hipoclorito de calcio recubierta vs. las muestras correspondientes sobre el cloro disponible y la clasificación División 5.1. En Tabla 4, las muestras 2 y 11 contienen hipoclorito de calcio ~68% AvCl, tamaño de partícula: ~200-2.000 µm. Muestras 12 y 13 contienen ~78% AvCl con tamaño de partícula: ~100 a 2.000.

Tabla 4. Comparación de la mezcla y oxidantes recubiertos no incluidos en la División 5.1

Muestra	Composición de Gránulos de Hipoclorito de Calcio Recubiertos			AvCl (%)	Humedad (%)	No incluido en la División 5.1
	Método	$Ca(OCl)_2 \cdot xH_2O$	Material de recubrimiento			
11	Mezclado	70%	30% $MgSO_4 \cdot 7H_2O$	47.6	19.6	SI
2	Recubri-miento	83%	0.7%NaOH + 14% $MgSO_4 \cdot xH_2O$ +2.5% poly(AM) $Na \cdot xH_2O$	55.9	13.8	SI
12	Mezclado	70%	30% $MgSO_4 \cdot 7H_2O$	54.4	24.1	SI
13	Recubri-miento	75%	0.6%NaOH + 25% $MgSO_4 \cdot xH_2O$	57.7	19.7	SI

Los resultados en Tabla 4 demuestran que las muestras recubiertas 2 y 13 no incluidas en la División 5.1 proporcionan cloro disponible más alto que las correspondientes muestras 11 y 12 mezcladas, incluidas en la División 5.1 (sic), incluso donde los contenidos de humedad de las muestras recubiertas son mucho menores que la muestra mezclada correspondiente.

Tabla 5 muestra los beneficios de tiempo de combustión relativo de otras muestras recubiertas con otros materiales de recubrimiento vs. sus muestras correspondientes. Se observaron tiempos de combustión más prolongados de las composiciones de hipoclorito de calcio recubiertas, basados en cloro disponible y componentes similares e idénticos, usados como materiales de recubrimiento, aunque los contenidos de humedad en

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las muestras recubiertas son inferiores a sus mezclas. En Tabla 5, cada muestra contiene hipoclorito de calcio: 68% de cloro disponible, tamaño de partícula: ~200-2.000 µm con ~6.6% de humedad.

Tabla 5. Comparación de Mezcla y Composición de Hipoclorito de Calcio Recubierta

Muestra #	Composición de Gránulos de Hipoclorito de Calcio Recubiertos			AvCl (%)	Humedad (%)	Tiempo de Combustión (segundos)
	Método	$Ca(OCl)_2 \cdot H_2O$	Material de Recubrimiento			
14	Mezcla	80%	20% $MgSO_4 \cdot xH_2O$	54.0	16.2	84
15	Recubrimiento		0.4%NaOH+16% $MgSO4 \cdot xH_2O$	56.1	13.0	100
16	Mezclado	80%	20%Na_3PO_4-$12H_2O$	54.0	16.2	62
17	Recubrimiento	83%	17%Na_3PO_4-$12H_2O$	55.4	14.1	83
18	Recubrimiento	82%	3%$Na_3PO_4 \cdot yH_2O$ + 6% $MgSO_4 \cdot xH_2O$ + 9% $CuSO_4 \cdot zH_2O$	54.7	12.2	81
19	Recubrimiento	83%	15%$Na_3PO_4 \cdot yH_2O$ + 2% poli(AM)Na·nH_2O*	55.7	13.7	90

* poli(AM)Na-nH_2O: sal de sodio de ácido poli(acrílico – ácido co-maleico) . nH2O

Por ejemplo, la muestra 15, recubierta con hidrato de sulfato de magnesio, muestra un tiempo de combustión 19% más prolongado que la muestra mezclada 14 con heptahidrato de sulfato de magnesio, en donde la muestra recubierta 15 tiene cloro disponible más alto y una humedad hidratada más baja. Análogamente, se observó un tiempo de combustión 34% más prolongado de la muestra recubierta 17 vs. la muestra mezclada 16 con dodecahidrato de fosfato de sodio.

Adicionalmente, se observó un tiempo de combustión más 30% más prolongado de la muestra recubierta multi-capa 18 con hidratos de fosfato

de sodio, sulfato de magnesio y sulfato de cobre, y la muestra 19 con hidratos de fosfato de sodio y poli(AM)Na vs. la muestra mezclada 16 con dodecahidrato de fosfato de sodio.

Para la caracterización de las ventajas de las muestras recubiertas se emplea en particular análisis SEM, EDS y XRD y las técnicas de mapa elemental.

Figura 2 muestra el análisis de mapa elemental de la muestra recubierta 3, y demuestra el recubrimiento uniforme multi-capa de las partículas con hipoclorito de calcio en la capa núcleo interior, cloruro de sodio en la capa intermedia e hidratos de sulfato de magnesio en la capa exterior.

Los análisis SEM y EDS muestran igualmente el recubrimiento multi-capa de la muestra 18, como se ilustra en la Figura 3 y 4 (sic). La Figura 4 ilustra que la muestra 18 se recubre con hidratos de sulfato de magnesio en la capa intermedia e hidratos de sulfato de cobre en la capa exterior. La imagen microscópica y el análisis EDS del recubrimiento con sección transversal de las partículas cortadas fueron reveladores como se muestra en las Figuras 3 y 4. El recubrimiento mostrado con un material de color azul (***"blue color material"***) en Figura 3 es hidrato de sulfato de cobre, y tiene alrededor de 25 µm de espesor sobre una partícula con un diámetro de alrededor de 1 mm. El análisis de mapa elemental muestra claramente dos capas con hidratos de sulfato de magnesio en la capa intermedia e hidratos de sulfato de cobre en la capa exterior. Se demostró que el recubrimiento con hidrato de sulfato de cobre fue más bien uniforme y tenía alrededor de 15-20 µm de espesor, mientras que el recubrimiento de hidrato de sulfato de magnesio fue el recubrimiento más variable y más delgado con alrededor de 7-15 µm de espesor.

Aunque la presente invención se dirige principalmente a tener hipoclorito de calcio hidratado o anhidro como materiales del núcleo y sales hidratadas como el material de recubrimiento, la invención puede abarcar también otras incorporaciones, donde los ingredientes activos ya mencionados son parte o la totalidad del material del núcleo.

Preferiblemente, otros oxidantes desinfectantes tales como ácido tricloroisocianúrico (TCCA), dicloroisocianurato de sodio (SDCC) y cloro- y bromohidantoínas, así como mezclas de oxidantes desinfectantes pueden ser útiles como tal material núcleo alternativo. Más aún, otros materiales de recubrimiento, tales como organometálicos, podrían utilizarse como materiales alternativos de recubrimiento en lugar de los materiales de sales ya mencionados. Más aún, la presente invención abarca igualmente el uso de otras técnicas de recubrimiento bien conocidas, tales como el empleo de partículas núcleo-corteza (***"core-shell particles"***) para elaborar las composiciones recubiertas. La composición de tales partículas núcleo-corteza podría variar desde un contenido medio de 10% de cloro (AvCl) hasta un contenido medio de 80% de cloro (AvCl).

Aunque esta invención se ha descrito anteriormente con referencia a incorporaciones específicas de la misma, es evidente que pueden introducirse muchos cambios, modificaciones y variaciones, sin apartarse del concepto inventivo divulgado en esta solicitud. En consecuencia, la invención pretende abarcar la totalidad de tales cambios, modificaciones y variaciones, que caen dentro del espíritu y ámbito amplio de las reivindicaciones adjuntas.

LO QUE SE REIVINDICA ES:

1. Una composición para tratamiento de agua, que contiene:

hipoclorito de calcio recubierto con un recubrimiento que incluye por lo menos una sal anhidra o hidratada;

en donde la citada composición contiene alrededor de 20% en peso a alrededor de 80% en peso de cloro disponible, basado en el peso total de la citada composición, y

en donde la citada composición contiene desde alrededor de 1% en peso a alrededor de 50% en peso de agua hidratada, basado en el peso total de la citada composición, y

en donde el citado recubrimiento contiene desde alrededor de 1% a alrededor de 80 % en peso del peso total de la citada composición, y

en donde la citada composición se clasifica como un oxidante no incluido en la División 5.1 o como un oxidante Clase 1 de la NFPA o Clase 2 de la NFPA.

2. La composición para tratamiento de agua de la reivindicación 1, en donde el citado hipoclorito de calcio contiene desde alrededor de 0% en peso a alrededor de 12 % en peso de agua, basado en el peso total del citado hipoclorito de calcio.

3. La composición para tratamiento de agua de la reivindicación 1, en donde el citado hipoclorito de calcio es una partícula que tiene un diámetro que varía desde alrededor de 40 a alrededor de 5.000 micrones.

4. La composición para tratamiento de agua de la reivindicación 3, en donde el citado hipoclorito de calcio es una partícula que tiene un diámetro que varía desde alrededor de 200 a alrededor de 5.000 micrones.

5. La composición para tratamiento de agua de la reivindicación 1, en donde la citada sal se selecciona del grupo conformado por sales

inorgánicas anhidras o hidratadas, sales orgánicas anhidras o hidratadas, sales poliméricas anhidras o hidratadas, y sus combinaciones.

6. La composición para tratamiento de agua de la reivindicación 5, en donde la citada sal hidratada se selecciona del grupo conformado por sales de metal alcalino y alcalinotérreo de haluros, sales de metal alcalino y alcalinotérreo de sulfato, sales de metal alcalino y alcalinotérreo de fosfato, sales de metal alcalino y alcalinotérreo de silicato, sales de metal alcalino y alcalinotérreo de borato, hidróxidos de metal alcalino y alcalinotérreo, y sus combinaciones.

7. La composición para tratamiento de agua de la reivindicación 5, en donde la citada sal hidratada se selecciona del grupo conformado por sulfatos de sodio, metaborato de litio, carbonato de sodio, ortofosfato de sodio, ortofosfato monohidrogenado de sodio, fosfato de sodio, pirofosfato de sodio, tetraborato de sodio, silicato de sodio, sulfato de aluminio, metasilicato de sodio, sulfato de aluminio y sodio, sulfato de magnesio, sulfato de potasio y aluminio, sulfato de zinc, sulfato de cobre, citrato de sodio, sal de sodio de ácido poli(acrílico – ácido maleico), y sus combinaciones.

8. La composición para tratamiento de agua de la reivindicación 1, en donde el citado recubrimiento contiene además uno o más ingredientes adicionales seleccionados del grupo conformado por purificadores de agua, inhibidores de costra de óxido, dispersantes, suavizantes de agua, inhibidores de la corrosión, alguicidas, fungicidas, aglutinantes, y sus combinaciones, y en donde los citados ingredientes adicionales están presentes en una cantidad que varía desde 0.1 a 5% en peso, basado en el peso total de la composición recubierta.

9. La composición para tratamiento de agua de la reivindicación 8, en donde los citados ingredientes adicionales se seleccionan del grupo

conformado por sulfato de cobre, sulfato de zinc, sulfato de aluminio, citrato de sodio, borato de sodio, tripolifosfato de sodio (STPP), hexametafosfato de sodio (SHMP), 1,3-dicloro-5,5-dimetilhidantoína (DCDMH), 1,3-dibromo-5,5dimetilhidantoína (DBDMH), 1-bromo-3-cloro-5,5-dimetilhidantoína (BCDMH), 1,3-dicloro-5-etil-5-metilhidantoína (DCEMH), 1,3-dibromo-5-etil-5-metilhidantoína (DBEMH), 1-bromo-3-cloro-5-metil-5-etilhidantoína (BCEMH), tricloro-, dicloro- y monoclorotriazina, bicloruro de dicloro-s-triazinatriona de sodio, su forma hidratada, y sus combinaciones.

10. La composición para tratamiento de agua de la reivindicación 1, en donde la citada composición contiene alrededor de 30% en peso a alrededor de 60 % en peso de cloro disponible, basado en el peso total de la citada composición.

11. La composición para tratamiento de agua de la reivindicación 1, en donde la citada composición contiene desde alrededor de 4% en peso a alrededor de 30% en peso de agua hidratada, basado en el peso total de la citada composición.

12. La composición para tratamiento de agua de la reivindicación 1, en donde la citada composición se forma en una tableta o briqueta.

13. La composición para tratamiento de agua de la reivindicación 1, en donde la citada sal es tetrahidrato de sulfato de magnesio.

14. Una composición para tratamiento de agua, que contiene:

(a) una capa núcleo interior que incluye hipoclorito de calcio;

(b) una o más capas intermedias situadas encima de la citada capa núcleo interior, comprendiendo la citada capa intermedia una o más sales inorgánicas anhidras o hidratadas, sales orgánicas anhidras o hidratadas, sales poliméricas anhidras o hidratadas, hidróxidos de metal alcalino,

hidróxidos de metal alcalinotérreo, y sus combinaciones, comprendiendo la citada capa intermedia desde alrededor de 1% a alrededor de 80% en peso del peso total de la citada composición; y

(c) una o más capas exteriores situadas encima de la(s) citada(s) capa(s) intermedia(s), comprendiendo las citadas capas exteriores por lo menos una sal anhidra o hidratada, incluyendo la citada capa exterior desde alrededor de 1% a alrededor de 35% en peso del peso total de la citada composición;

en donde la citada composición contiene alrededor de 20% en peso a alrededor de 80 % en peso de cloro disponible, basado en el peso total de la citada composición;

en donde la citada composición contiene desde alrededor de 1% en peso a alrededor de 50 % en peso de agua hidratada, basado en el peso total de la citada composición;

y en donde la citada composición se clasifica como un oxidante no incluido en la División 5.1 o un oxidante Clase 1 de la NFPA o un oxidante Clase 2 de la NFPA.

15. La composición para tratamiento de agua de la reivindicación 14, en donde el citado hipoclorito de calcio contiene desde alrededor de 0% en peso a alrededor de 12% en peso de agua, basado en el peso total del citado hipoclorito de calcio.

16. La composición para tratamiento de agua de la reivindicación 14, en donde el citado hipoclorito de calcio es una particula que tiene un diámetro que varía desde alrededor de 40 a alrededor de 5.000 micrones.

17. La composición para tratamiento de agua de la reivindicación 16, en donde el citado hipoclorito de calcio es una partícula que tiene un diámetro que varía desde alrededor de 200 a alrededor de 5.000 micrones.

18. La composición para tratamiento de agua de la reivindicación 14, en donde la sal anhidra o hidratada en la citada capa exterior se selecciona del grupo conformado por sales inorgánicas anhidras o hidratadas, sales orgánicas anhidras o hidratadas, sales poliméricas anhidras o hidratadas, y sus combinaciones.

19. La composición para tratamiento de agua de la reivindicación 18, en donde la citada sal hidratada se selecciona del grupo conformado por sales de metal alcalino y alcalinotérreo de haluros, sales de metal alcalino y alcalinotérreo de sulfato, sales de metal alcalino y alcalinotérreo de fosfato, sales de metal alcalino y alcalinotérreo de silicato, sales de metal alcalino y alcalinotérreo de borato, hidróxidos de metal alcalino y alcalinotérreo, y sus combinaciones.

20. La composición para tratamiento de agua de la reivindicación 18, en donde la citada sal hidratada se selecciona del grupo conformado por sulfatos de sodio, metaborato de litio, carbonato de sodio, ortofosfato de sodio, ortofosfato monohidrogenado de sodio, fosfato de sodio, pirofosfato de sodio, tetraborato de sodio, silicato de sodio, sulfato de aluminio, metasilicato de sodio, sulfato de aluminio y sodio, sulfato de magnesio, sulfato de potasio y aluminio, sulfato de zinc, sulfato de cobre, citrato de sodio, sal de sodio de ácido poli(acrílico – ácido maleico), y sus combinaciones.

21. La composición para tratamiento de agua de la reivindicación 14, en donde las citadas una o más capas exteriores contienen además uno o más ingredientes adicionales seleccionados del grupo conformado por purificadores de agua, inhibidores de costra de óxido, dispersantes, suavizantes de agua, inhibidores de la corrosión, alguicidas, fungicidas, aglutinantes, y sus combinaciones, y en donde los citados ingredientes adicionales están presentes en una cantidad que varía desde 0.1 a 5% en peso, basado en el peso total de la composición recubierta.

22. La composición para tratamiento de agua de la reivindicación 21, en donde la citada capa exterior contiene además uno o más agentes adicionales seleccionados del grupo conformado por sulfato de cobre, sulfato de zinc, sulfato de aluminio, citrato de sodio, borato de sodio, tripolifosfato de sodio (STPP), hexametafosfato de sodio (SHMP), 1,3-dicloro-5,5-dimetilhidantoína (DCDMH), 1,3-dibromo-5,5dimetilhidantoína (DBDMH), 1-bromo-3-cloro-5,5-dimetilhidantoína (BCDMH), 1,3-dicloro-5-etil-5-metilhidantoína (DCEMH), 1,3-dibromo-5-etil-5-metilhidantoína (DBEMH), 1-bromo-3-cloro-5-metil-5-etilhidantoína (BCEMH), tricloro-, dicloro- y monoclorotriazina, bicloruro de dicloro-s-triazinatriona de sodio, su forma hidratada, y sus combinaciones, y en donde los citados ingredientes adicionales están presentes en una cantidad que varía desde 0.1 a 5% en peso, basado en el peso total de la composición recubierta.

23. La composición para tratamiento de agua de la reivindicación 14, en donde la citada sal inorgánica en la citada capa intermedia contiene cloruro de metal alcalino, sulfatos de metal alcalino, fosfatos de metal alcalino, silicatos de metal alcalino, boratos de metal alcalino, y sus combinaciones.

24. La composición para tratamiento de agua de la reivindicación 14, en donde la capa intermedia es una sal seleccionada del grupo conformado por cloruro de sodio, sulfato de sodio, borato de sodio, silicato de sodio, hidróxido de litio, hidróxido de calcio, y sus combinaciones.

25. La composición para tratamiento de agua de la reivindicación 14, en donde la citada composición contiene alrededor de 30% en peso a alrededor de 60 % en peso de cloro disponible, basado en el peso total de la citada composición.

26. La composición para tratamiento de agua de la reivindicación 14, en donde la citada composición contiene desde alrededor de 4% en peso a

alrededor de 30% en peso de agua hidratada, basado en el peso total de la citada composición.

27. La composición para tratamiento de agua de la reivindicación 14, en donde la citada composición se forma en una tableta o briqueta.

28. La composición para tratamiento de agua de la reivindicación 14, en donde la citada sal es tetrahidrato de sulfato de magnesio.

29. La composición para tratamiento de agua de la reivindicación 14, en donde la citada capa exterior contiene una sal polimérica que incluye desde alrededor de 0.5% a alrededor de 15% en peso del peso total de la citada composición.

UN HIPOCLORITO DE CALCIO RECUBIERTO MULTI-CAPA

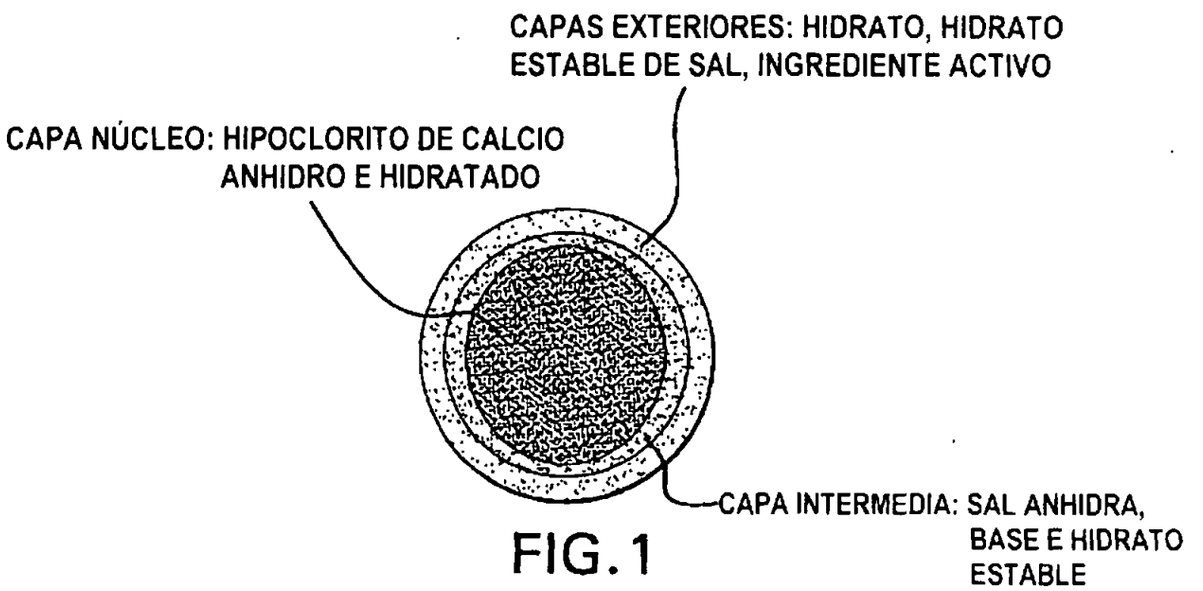


FIG. 1

ANÁLISIS DE MAPA ELEMENTAL DE LA MUESTRA RECUBIERTA 3

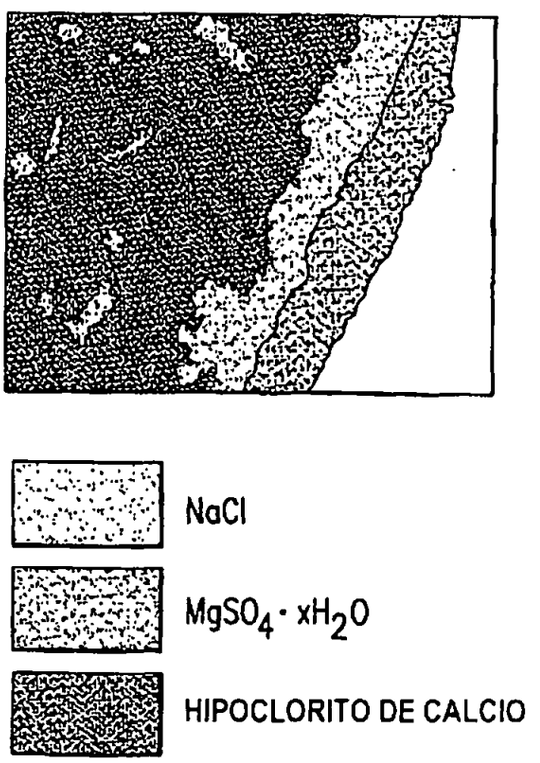
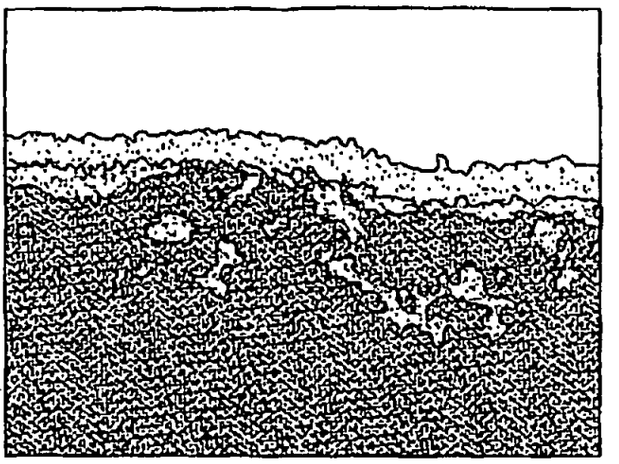


FIG. 2

IMAGEN DE LA MUESTRA RECUBIERTA 16



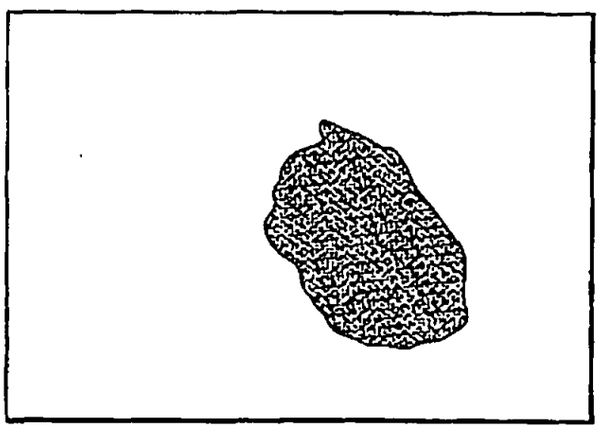
SULFATO DE COBRE •zH_2O

SULFATO DE MAGNESIO •zH_2O

HIPOCLORITO DE CALCIO

FIG.3

ANÁLISIS DE MAPA ELEMENTAL DE LA MUESTRA RECUBIERTA 16



HIPOCLORITO DE CALCIO

FIG.4

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PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To: Todd E. Garabedian
Wiggin and Dana LLP
One Century Tower
New Haven, Connecticut 06508-1832

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

	Date of mailing *(day/month/year)* 03 AUG 2007
Applicant's or agent's file reference 102782-201	**FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US 06/45645	International filing date *(day/month/year)* 29 November 2006 (29.11.2006)
Applicant Arch Chemicals, Inc.	

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

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

   When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

   Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Facsimile No.: +41 22 740 14 35

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

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

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

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

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

4. **Reminders**

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

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

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

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

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

Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/220 (January 2004) *(See notes on accompanying sheet)*

RECEIVED 8/7/07

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 102782-201	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US 06/45645	International filing date *(day/month/year)* 29 November 2006 (29.11.2006)	(Earliest) Priority Date *(day/month/year)* 01 December 2005 (01.12.2005)
Applicant Arch Chemicals, Inc.		

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

This international search report consists of a total of 2 sheets.

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

1. **Basis of the report**

a With regard to the **language**, the international search was carried out on the basis of:

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

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

b. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II)

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

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,

a. the figure of the drawings to be published with the abstract is Figure No. 1

☒ as suggested by the applicant

☐ as selected by this Authority, because the applicant failed to suggest a figure

☐ as selected by this Authority, because this figure better characterizes the invention

b. ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 06/45645

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C11D 3/00 (2007.01)
USPC 510/375
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC 510/375

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC 510/375; 423/474; 252/186.36, 252/186.37, 252/187.27, 252/187.28, 252/187.29, 252/187.3 (text search - see terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST (PGPB,USPT,USOC,EPAB,JPAB); Google
Search Terms: calcium hypochlorite, salt, available chlorine, polymeric salt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ------ Y	US 4,201,756 A (Saeman et al.) 06 May 1980 (06.05.1980) Abstract; col 4, ln 10 to col 5, ln 36; col 5, ln 34-36; col 16, ln 44 to col 17, ln 24; col 18, ln 10-59; col 27, ln 5-19	1-7, 10-11, 13-20, 23-26, 28-29 ---------- 8-9, 12, 21-22 and 27
Y	US 5,164,109 A (Wojlowicz) 17 November 1992 (17.11.1992) col 2, ln 18-46; col 3, ln 6-7; col 4, ln 8-12	8-9, 12, 21-22 and 27
A	US 2004/0214738 A1 (Brennan et al.) 28 October 2004 (28.10.2004) para [0013]-[0015]	1-29

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 June 2007 (03.06.2007)	03 AUG 2007
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: Todd E. Garabedian
Wiggin and Dana LLP
One Century Tower
New Haven, Connecticut 06508-1832

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	03 AUG 2007
Applicant's or agent's file reference 102782-201	FOR FURTHER ACTION See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US 06/45645	29 November 2006 (29.11.2006)	01 December 2005 (01.12.2005)

International Patent Classification (IPC) or both national classification and IPC
IPC(8) - C11D 3/00 (2007.01)
USPC - 510/375

Applicant Arch Chemicals, Inc.

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

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

2. FURTHER ACTION

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

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

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

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

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	30 May 2007 (30.05.2007)	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/237 (cover sheet) (April 2005)

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 06/45645

Box No. I Basis of this opinion

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

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

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

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

   a. type of material

      ☐ a sequence listing

      ☐ table(s) related to the sequence listing

   b. format of material

      ☐ on paper

      ☐ in electronic form

   c. time of filing/furnishing

      ☐ contained in the international application as filed

      ☐ filed together with the international application in electronic form

      ☐ furnished subsequently to this Authority for the purposes of search

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

4. Additional comments:

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 06/45645

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

1. Statement

Novelty (N)	Claims	8-9, 12-13, 21-22, 27-28	YES
	Claims	1-7, 10-11, 14-20, 23-26 and 29	NO
Inventive step (IS)	Claims	none	YES
	Claims	1-29	NO
Industrial applicability (IA)	Claims	1-29	YES
	Claims	none	NO

2. Citations and explanations:

Claims 1-7, 10-11, 14-20, 23-26 and 29 lack novelty under PCT Article 33(2) as being anticipated by US 4,201,756 A to Saeman et al. (hereinafter 'Saeman')

As to claims 1-2 and 10-11, Saeman teaches a water treatment composition (col 4, ln 10 to col 5, ln 36), comprising:
calcium hypochlorite coated with a coating comprising at least one hydrated or
anhydrous salt (col 4, ln 10-14);
wherein said composition contains about 20 wt% to about 80 wt% or 30-60 wt% available chlorine based on the total weight of said composition (col 4, ln 25-26), and
wherein said composition contains from about 1 wt% to about 50 wt% , 0-12 wt%, or 4-30 wt% of hydrated water based on the total weight of said composition(col 4, ln 24-25), and
wherein said coating comprises from about 1 % to about 80 wt% of the total weight of said composition (4-45 %; col 18, ln 55-59), and wherein said composition is classified as a non Division 5.1 oxidizer or as a NFPA Class 1 or NFP A Class 2 oxidizer (when the particles have a coating of an inorganic salt as the exterior layer, there is an increased degree of resistance to ignition; col 5, ln 34-36; meets the NFPA Class 1 requirements).

As to claims 3-4, in addition to the above arguments for claim 1, Saeman teaches the calcium hypochlorite is a particle having a diameter ranging from about 40 to about 5000 microns or 200-5000 microns (200-2000 microns; col 4, ln 16-17).

As to claim 5, in addition to the above arguments for claim 1, Saeman teaches the salt is selected from the
group consisting of hydrated or anhydrous inorganic salts (col 4, ln 14), hydrated or anhydrous organic salts, hydrated or anhydrous polymeric salts(col 27, ln 5-19), and combinations thereof.

As to claim 6, in addition to the above arguments for claim 5, Saeman teaches said hydrated salt is selected from the group consisting of alkaline and alkaline earth metal salts of halides, alkaline and alkaline earth metal salts of sulfate, alkaline and alkaline earth metal salts of phosphate, alkaline and alkaline earth metal salts of silicate, alkaline and alkaline earth metal salts of borate, alkaline and alkaline earth metal hydroxides, and combinations thereof (Abstract).

As to claim 7, in addition to the above arguments for claim 5, Saeman teaches said hydrated salt is selected
from the group consisting of sodium sulfates, lithium metaborate, sodium carbonate, sodium orthophosphate, sodium monohydrogen orthophosphate, sodium phosphate, sodium pyrophosphate, sodium tetraborate, sodium silicate, aluminum sulfate, sodium metasilicate, sodium aluminum sulfate, magnesium sulfate, aluminum potassium sulfate, zinc sulfate, copper sulfate, sodium citrate, poly(acrylic acid-maleic acid) sodium salt, and
combinations thereof (col 16, ln 44-48).

As to claims 14-15 and 25-26, Saeman teaches a water treatment composition(col 4, ln 10 to col 5, ln 36), comprising:
- an inner core layer comprising calcium hypochlorite (col 4, ln 13);
- one or more interlayers positioned on top of said inner core layer, said interlayer comprising one or more hydrated or anhydrous inorganic salts (col 4, ln 14), hydrated or anhydrous organic salts, hydrated or anhydrous polymeric salts(col 27, ln 5-19), alkaline metal hydroxides, alkaline earth hydroxides, and combinations thereof (Abstract), said interlayer comprising from about 1 % to about 80 wt% of the total weight of said composition(col 18, ln 55-59); and
- one or more outer layers positioned on top of said interlayer(s), said outer layers comprising at least one hydrated or anhydrous salt, said outer layer comprising from about 1% to about 35 wt% of the total weight of said composition(col 18, ln 13-17);
wherein said composition contains about 20 wt% to about 80 wt% or 30-60% available chlorine based on the total weight of said composition(col 4, ln 25-26);
said composition contains from about 1 wt% to about 50 wt%, 1-12% or 4-30% of hydrated water based on the total weight of said composition (col 4, ln 24-25); and
wherein said composition is classified as a non Division 5.1 oxidizer or as a NFP A Class 1 or NFPA Class 2 oxidizer(when the particles have a coating of an inorganic salt as the exterior layer, there is an increased degree of resistance to ignition; col 5, ln 34-36; meets the NFPA Class 1 requirements).

As to claims 16-17, in addition to the above arguments for claim 14, wherein said calcium hypochlorite is a particle having a diameter ranging from about 40 to about 5000 microns or 200-5000 microns (col 4, ln 16-17).

--Please See Continuation Sheet--

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 06/45645

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V. 2. Citations and explanations:

As to claim 18, in addition to the above arguments for claim 14, Saeman teaches the salt is selected from the group consisting of hydrated or anhydrous inorganic salts (col 4, ln 14), hydrated or anhydrous organic salts, hydrated or anhydrous polymeric salts(col 27, ln 5-19), and combinations thereof.

As to claim 19, in addition to the above arguments for claim 18, Saeman teaches said hydrated salt is selected from the group consisting of alkaline and alkaline earth metal salts of halides, alkaline and alkaline earth metal salts of sulfate, alkaline and alkaline earth metal salts of phosphate, alkaline and alkaline earth metal salts of silicate, alkaline and alkaline earth metal salts of borate, alkaline and alkaline earth metal hydroxides, and combinations thereof (Abstract).

As to claim 20, in addition to the above arguments for claim 18, Saeman teaches said hydrated salt is selected from the group consisting of sodium sulfates, lithium metaborate, sodium carbonate, sodium orthophosphate, sodium monohydrogen orthophosphate, sodium phosphate, sodium pyrophosphate, sodium tetraborate, sodium silicate, aluminum sulfate, sodium metasilicate, sodium aluminum sulfate, magnesium sulfate, aluminum potassium sulfate, zinc sulfate, copper sulfate, sodium citrate, poly(acrylic acid-maleic acid) sodium salt, and combinations thereof (col 16, ln 44-48).

As to claim 23, in addition to the above arguments for claim 14, Saeman teaches said inorganic salt in said interlayer comprises alkaline metal chlorides, alkaline metal sulfates, alkaline metal phosphates, alkaline metal silicates, alkaline metal borates, and combinations thereof (Abstract).

As to claim 24, in addition to the above arguments for claim 14, Saeman teaches an interlayer is a salt selected from the group consisting of sodium chloride, sodium sulfate, sodium borate, sodium silicate, lithium hydroxide, calcium hydroxide, and combinations thereof(col 16, ln 49 to col 17, ln 24).

As to claim 29, in addition to the above arguments for claim 14, Saeman teaches an outer layer comprising a polymeric salt comprising from about 0.5% to about 15 wt% of the total weight of said composition (col 27 ln 5-19).

Claims 13 and 28 lack an inventive step under PCT Article 33(3) as being obvious over Saeman.

As to claims 13 and 28, in addition to the above arguments for claims 1 and 14, Saeman teaches said salt is magnesium sulfate hydrate from 4 to 7 moles of water (col 18, ln 10). This would have made magnesium sulfate tetrahydrate obvious to one skilled in the art.

Claims 8-9, 12, 21-22 and 27 lack an inventive step under PCT Article 33(3) as being obvious over Saeman in view of US 5,164,109 A (Wojtowicz).

As to claims 8 and 21, in addition to the above arguments for claims 1 and 14, Wojtowicz teaches a coating further comprises one or more additional ingredients selected from the group consisting of scale inhibitors (col 4, ln 8-12) and algaecides (col 2, ln 37-46) in an amount ranging from 0.1 to 5 wt%, based on the total weight of the coated composition (1-40 %; col 2, ln 33-34). It would have been obvious to one skilled in the art to combine these references to develop a water treatment composition made up of calcium hypochlorite and other salts.

As to claims 9 and 22, in addition to the above arguments for claims 8 and 21, Wojtowicz teaches said additional ingredients are zinc sulfate or its hydrated form, and combinations thereof (col 2, ln 18-26).

As to claims 12 and 27, in addition to the above arguments for claims 1 and 14, Wojtowicz teaches said composition is formed into a tablet or briquette (col 3, ln 6-7).

Claims 1-29 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

(i) the claim is unchanged;
(ii) the claim is cancelled;
(iii) the claim is new;
(iv) the claim replaces one or more claims as filed;
(v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under Article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments and any accompanying statement, under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the time of filing the amendments (and any statement) with the International Bureau, also file with the International Preliminary Examining Authority a copy of such amendments (and of any statement) and, where required, a translation of such amendments for the procedure before that Authority (see Rules 55.3(a) and 62.2, first sentence). For further information, see the Notes to the demand form (PCT/IPEA/401).

If a demand for international preliminary examination is made, the written opinion of the International Searching Authority will, except in certain cases where the International Preliminary Examining Authority did not act as International Searching Authority and where it has notified the International Bureau under Rule 66.1*bis*(b), be considered to be a written opinion of the International Preliminary Examining Authority. If a demand is made, the applicant may submit to the International Preliminary Examining Authority a reply to the written opinion together, where appropriate, with amendments before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later (Rule 43*bis*.1(c)).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see the *PCT Applicant's Guide*, Volume II.

NOTES TO FORM PCT/ISA/220

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

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

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

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

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

What parts of the international application may be amended ?

Under Article 19, only the claims may be amended.

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

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

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

Where not to file the amendments ?

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

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

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

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

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

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

What documents must/may accompany the amendments ?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

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

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

Europäisches Patentamt
European Patent Office
Office européen des brevets

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2280 HV RIJSWIJK
NETHERLANDS
Tel. +31 (0)70 340-2040
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APR 21 2008
By

For any questions about this communication:
Tel.:+31 (0)70 340 45 00

102372-201

Date
11.04.08

Reference	Application No./Patent No.
	06838546.7 - 1215 PCT/US2006045645
Applicant/Proprietor	
Arch Specialty Chemicals, Inc.	

Entry into the European phase before the European Patent Office

The following information describes the procedural steps required for entry into the European phase before the European Patent Office (EPO). You are advised to read it carefully because failure to take the necessary action in due time can lead to a loss of rights.

1. The above mentioned international patent application has been given the **European application No. 06838546.7**.

2. Applicants **without a residence or their principal place of business** in an EPC Contracting State may themselves initiate European processing of their international applications, provided they do so before expiry of the 31st month from the priority date.

   During the European phase before the EPO as designated or elected Office, however, such applicants **must** be represented by a professional representative (Art. 133(2) and Art. 134(1) and (8) EPC).

   Where, at the expiry of the time period laid down in Rule 163(5) EPC, the requirements of Article 133(2) EPC have not been complied with, the European patent application will be **refused**, pursuant to Rule 163(6) EPC.

   Please note that a professional representative authorised to act before the EPO and who acted for the applicant during the international phase does not automatically become the representative for the European phase. Applicants are therefore strongly advised to appoint in good time any representative they wish to initiate the European phase for them; otherwise the EPO has to send all communications directly to the applicant.

3. Applicants **with a residence or their principal place of business** in an EPC Contracting State are not obliged to appoint for the European phase a professional representative authorised to act before the EPO. However, in view of the complexity of the procedure it is recommended that they do so.

4. Applicants and professional representatives are also strongly advised to initiate the European phase using **EPO Form 1200**. It is available free of charge from the EPO or via the EPO website at **http://www.epo.org**. Similarly, it can be or generated with the epoline® Online Filing Software, obtainable free of charge from the EPO (**http://www.epoline.org**) The use of the form is not compulsory.

5. Where the EPO is acting as designated or elected Office (Art. 22(1) and (3) and Art. 39(1) PCT), to enter the European phase before the EPO, the **following acts** must be performed by the applicant **within 31 months** from the date of filing of the international application or (where applicable) the earliest priority date:

   a) Supply a translation of the international application into an EPO official language, if the International Bureau did not publish the application in such language (Art. 22(1) PCT and R. 159(1)(a) EPC);

   b) Specify the application documents, as originally filed or as amended, on which the European grant procedure is to be based (R. 159(1)(c) EPC);

   c) Pay the filing fee and, where a supplementary European search report has to be drawn up, the search fee (R. 159(1)(c) and (e) EPC);

   d) Pay the designation fee for each designated Contracting State if the time limit laid down in Rule 39(1) EPC (i.e. six months after publication of the international search report) has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(d) EPC);

   e) File the request for examination if the time limit laid down in Rule 70(1) EPC (i.e. six months after publication of the international search report) has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(f) EPC);

   f) Pay the renewal fee in respect of the third year, if the fee has fallen due (see Rule 51(1) EPC) before expiry of the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(g) EPC);

   g) File, where applicable, the certificate of exhibition referred to in Article 55(2) and Rule 25 EPC (R. 159(1)(h) EPC);

   h) Pay the claims fees for the sixteenth and each subsequent claim when the application documents on which the European grant procedure is to be based comprise more than fifteen claims (R. 162(1) EPC).

If either the translation of the international application or the request for examination is not filed in due time, or if the filing fee or the search fee is not paid in due time, or no designation fee is paid in due time, the European patent application **shall be deemed to be withdrawn** (R. 160(1) EPC).

If the renewal fee is not paid in due time, it may still be paid within six months of the due date, provided that an additional fee is also paid within that period (R. 51(2) EPC).

If the claims fees are not paid in due time, they may still be paid within one month from a communication of the EPO pointing out the failure to observe the time limit (R. 162(2) EPC).

6. For an overview of search and examination fees, see the Notice from the European Patent Office dated 1 March 2006 (OJ EPO 2006, 192). The amounts of the fees are regularly published in the Official Journal of the EPO and are available on the EPO internet site at **http://www.epo.org**. At any time, payments to the EPO can be validly made by anybody.

7. If the applicant had appointed a representative during the application's international phase, the present Form will be sent to the representative, asking him to inform the applicant accordingly.

   All subsequent communications will be sent to the applicant, or if the EPO is informed of his appointment in time, to the applicant's European representative.

8. For more details about time limits and procedural acts before the EPO as designated or elected Office, see the EPO brochure "How to get an European patent", Guide for applicants - Part 2, PCT procedure before the EPO - "Euro-PCT" (EPO PCT Guide). This brochure, the list of professional representatives before the EPO, Form 1200 and details of the latest fees are available on the Internet under **http://www.epo.org**.

Receiving Section

WO 2007/064681
PCT/US2006/045645

PATENT COOPERATION TREA[illegible]

From the INTERNATIONAL BUREAU

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PCT

SECOND AND SUPPLEMENTARY NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO DESIGNATED OFFICES WHICH APPLY THE 30 MONTH TIME LIMIT UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:

GARABEDIAN, Todd, E.
WIGGIN AND DANA LLP
One Century Tower
New Haven, CT 06508-1832
ETATS-UNIS D'AMERIQUE

RECEIVED
APR
By

Date of mailing *(day/month/year)* 03 April 2008 (03.04.2008)	
Applicant's or agent's file reference 102782-201	IMPORTANT NOTICE

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2006/045645	29 November 2006 (29.11.2006)	01 December 2005 (01.12.2005)

Applicant

ARCH CHEMICALS, INC.

1. **ATTENTION:** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does not apply**, please see Form PCT/IB/308(First Notice) issued previously.

2. Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93*bis*.1. The International Bureau has effected that communication on the date indicated below:
07 June 2007 (07.06.2007)

AU, AZ, BY, CN, CO, DZ, EP, HU, KG, KP, KR, MD, MK, MY, MZ, NA, NG, PG, RU, SY, TM, US

In accordance with Rule 47.1(c-*bis*)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

3. The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93*bis*.1 :

AE, AG, AL, AM, AP, AT, BA, BB, BG, BR, BW, BZ, CA, CR, CU, CZ, DE, DK, DM, EA, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, ID, IL, IN, IS, JP, KE, KM, KN, KZ, LA, LC, LK, LR, LS, LT, LV, LY, MA, MG, MN, MW, MX, NI, NO, NZ, OA, OM, PH, PL, PT, RO, RS, SC, SD, SE, SG, SK, SL, SM, SV, TJ, TN, TR, TT, UA, UZ, VC, VN, ZA, ZM, ZW

In accordance with Rule 47.1(c-*bis*)(iii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

4. **TIME LIMITS for entry into the national phase**

For the designated or elected Office(s) listed above, the applicable time limit for entering the national phase will, subject to what is said in the following paragraph, be 30 **MONTHS** from the priority date.

In practice, time limits other than the 30-month time limit will continue to apply, for various periods of time, in respect of certain of the designated or elected Office(s) listed above. For regular updates on the applicable time limits (30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at http://www.wipo.int/pct/en/index.html.

It is the applicant's sole responsibility to monitor all these time limits.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer

Athina Nickitas-Etienne

e-mail: pt04.pct@wipo.int

PATENT COOPERATION TRE Y

WO 2007/064681
PCT/US2006/04564

From the INTERNATIONAL BUREAU

97

PCT

NOTIFICATION CONCERNING
AVAILABILITY OF THE PUBLICATION
OF THE INTERNATIONAL APPLICATION

To:

GARABEDIAN, Todd, E.
WIGGIN AND DANA LLP
One Century Tower
New Haven, CT 06508-1832
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)*	
22 November 2007 (22.11.2007)	
Applicant's or agent's file reference	IMPORTANT NOTICE
102782-201	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2006/045645	29 November 2006 (29.11.2006)	01 December 2005 (01.12.2005)

Applicant

ARCH CHEMICALS, INC.

The applicant is hereby **notified** that the International Bureau:

☐ has **published** the above-indicated international application on under No. WO

☑ has **republished** the above-indicated international application on 22 November 2007 (22.11.2007) under No. WO 2007/064681
For an explanation as to the reason for this republication of the international application, reference is made to INID codes (15), (48) or (88) (*as the case may be*) on the front page of the published international application.

A copy of the international application is available for viewing and downloading on WIPO's website at the following address: http://www.wipo.int/pctdb (under "Query" enter the PCT or WO number).

The applicant may also request a paper copy of the published international application from the International Bureau by submitting a written request to PatentScope@wipo.int or to the address provided below.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer

Yoshiko Kuwahara

e-mail: pt07.pct@wipo.int

From the INTERNATIONAL BUREAU

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PCT

FIRST NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO DESIGNATED OFFICES WHICH DO NOT APPLY THE 30 MONTH TIME LIMIT UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:

GARABEDIAN, Todd, E.
WIGGIN AND DANA LLP
One Century Tower
New Haven, CT 06508-1832
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)* 05 July 2007 (05.07.2007)	
Applicant's or agent's file reference 102782-201	IMPORTANT NOTICE

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2006/045645	29 November 2006 (29.11.2006)	01 December 2005 (01.12.2005)

Applicant

ARCH CHEMICALS, INC.

1. **ATTENTION:** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does apply**, please see Form PCT/IB/308(Second and Supplementary Notice) (to be issued promptly after the expiration of 28 months from the priority date).

2. Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93*bis*.1. The International Bureau has effected that communication on the date indicated below:
07 June 2007 (07.06.2007)

   None

   In accordance with Rule 47.1(c-*bis*)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

3. The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93*bis*.1 :

   CH, LU, SE, TZ, UG

   In accordance with Rule 47.1(c-*bis*)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

4. **TIME LIMITS for entry into the national phase**

   For the designated Office(s) listed above, and unless a demand for international preliminary examination has been filed before the expiration of **19 months** from the priority date (see Article 39(1)), the applicable time limit for entering the national phase will, subject to **what is said in the following paragraph**, be **20 MONTHS** from the priority date.

   In practice, **time limits other than the 20-month time limit** will continue to apply, for various periods of time, in respect of certain of the designated Offices listed above. For **regular updates on the applicable time limits** (20 or 21 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at http://www.wipo.int/pct/en/index.html.

   It is the applicant's sole **responsibility** to monitor all these time limits.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer

Yoshiko Kuwahara

e-mail: pt07.pct@wipo.int

PATENT COOPERATION TREA

From the INTERNATIONAL BUREAU

95

PCT

NOTIFICATION CONCERNING AVAILABILITY OF THE PUBLICATION OF THE INTERNATIONAL APPLICATION

To:

GARABEDIAN, Todd, E.
WIGGIN AND DANA LLP
One Century Tower
New Haven, CT 06508-1832
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)* 07 June 2007 (07.06.2007)	
Applicant's or agent's file reference 102782-201	IMPORTANT NOTICE

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2006/045645	29 November 2006 (29.11.2006)	01 December 2005 (01.12.2005)

Applicant
ARCH CHEMICALS, INC.

The applicant is hereby **notified** that the International Bureau:

☑ has **published** the above-indicated international application on 07 June 2007 (07.06.2007) under No. WO 2007/064681

☐ has **republished** the above-indicated international application on under No. WO
For an explanation as to the reason for this republication of the international application, reference is made to INID codes (15), (48) or (88) *(as the case may be)* on the front page of the published international application.

A copy of the international application is available for viewing and downloading on WIPO's website at the following address: http://www.wipo.int/pctdb (under "Query" enter the PCT or WO number).

The applicant may also request a paper copy of the published international application from the International Bureau by submitting a written request to PatentScope@wipo.int or to the address provided below.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer
Yoshiko Kuwahara

e-mail: pt07.pct@wipo.int

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From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

GARABEDIAN, Todd, E.
WIGGIN AND DANA LLP
One Century Tower
New Haven, CT 06508-1832
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)* 06 February 2007 (06.02.2007)	
Applicant's or agent's file reference 102782-201	IMPORTANT NOTIFICATION
International application No. PCT/US2006/045645	International filing date *(day/month/year)* 29 November 2006 (29.11.2006)
International publication date *(day/month/year)* **Not yet published**	Priority date *(day/month/year)* 01 December 2005 (01.12.2005)
Applicant ARCH CHEMICALS, INC.	

1. By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).

2. *(If applicable)* The **letters "NR"** appearing in the right-hand column denote a **priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau** under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

3. *(If applicable)***An asterisk (*)** appearing next to a date of receipt, in the right-hand column, denotes a **priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b)** (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
01 December 2005 (01.12.2005)	60/741,503	US	16 January 2007 (16.01.2007)
21 November 2006 (21.11.2006)	11/602,816	US	16 January 2007 (16.01.2007)

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From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

GARABEDIAN, Todd, E.
WIGGIN AND DANA LLP
One Century Tower
New Haven, CT 06508-1832
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)* 06 February 2007 (06.02.2007)	
Applicant's or agent's file reference 102782-201	IMPORTANT NOTIFICATION
International application No. PCT/US2006/045645	International filing date *(day/month/year)* 29 November 2006 (29.11.2006)
International publication date *(day/month/year)* Not yet published	Priority date *(day/month/year)* 01 December 2005 (01.12.2005)
Applicant ARCH CHEMICALS, INC.	

1. By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).

2. *(If applicable)* The letters **"NR"** appearing in the right-hand column denote a **priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau** under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, **the attention of the applicant is directed to Rule** 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

3. *(If applicable)***An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b)** (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
01 December 2005 (01.12.2005)	60/741,503	US	16 January 2007 (16.01.2007)
21 November 2006 (21.11.2006)	11/602,816	US	16 January 2007 (16.01.2007)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer
Yoshiko Kuwahara
Facsimile No. +41 22 338 90 84
Telephone No. +41 22 338 91 76

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From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF RECEIPT OF RECORD COPY

(PCT Rule 24.2(a))

GARABEDIAN, Todd, E.
WIGGIN AND DANA LLP
One Century Tower
New Haven, CT 06508-1832
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)*	IMPORTANT NOTIFICATION
05 February 2007 (05.02.2007)	
Applicant's or agent's file reference	International application No.
102782-201	PCT/US2006/045645

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

ARCH CHEMICALS, INC. (for all designated States except US)

International filing date: 29 November 2006 (29.11.2006)

Priority date(s) claimed: 01 December 2005 (01.12.2005)
21 November 2006 (21.11.2006)

Date of receipt of the record copy by the International Bureau: 17 January 2007 (17.01.2007)

List of designated Offices:

AP: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW
EA: AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
EP: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
OA: BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
National: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

ATTENTION: The applicant should carefully check the data appearing in this notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau. **In addition, the applicant's attention is drawn to the information contained in the Annex**, relating to:

- time limits for entry into the national phase - **see updated Important information (as of April 2002)**
- requirements regarding priority documents (if applicable)

A copy of this notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Roux Marianne
Facsimile No. +41 22 338 82 70	Facsimile No. +41 22 338 90 90 Telephone No. +41 22 338 95 74

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INFORMATION ON ENTERING THE NATIONAL PHASE

The applicant is reminded that the **"national phase" must be entered** before each of the designated Offices indicated on the cover sheet of this notification by paying national fees and furnishing translations, as prescribed by Articles 22 and 39 and the applicable national laws. In addition, the applicant may also have to comply with **other special requirements** applicable in certain Offices. It is the **applicant's responsibility** to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most Offices do not issue reminders to applicants in connection with the entry into the national phase.

The applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date, not only in respect of any elected Office if a demand for international preliminary examination is filed before the expiration of 19 months from the priority date (see Article 39(1)), but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see *PCT Gazette* No. 44/2001 of 1 November 2001, pages 19926, 19932 and 19934, as well as the *PCT Newsletter*, October and November 2001 and February 2002 issues.

In practice, **time limits other than the 30-month time limit will continue to apply, for various periods of time**, in respect of certain designated or elected Offices. For **regular updates on the applicable time limits (20, 21, 30 or 31 months, or other time limit)**, Office by Office, refer to the *PCT Gazette* ("Section IV" part published on a weekly basis), to the *PCT Newsletter* (on a monthly basis) and to the relevant National Chapters in Volume II of the *PCT Applicant's Guide* (the paper version of which is updated usually twice a year and the Internet version of which is updated usually on a weekly basis). Finally, a cumulative table of all applicable time limits for entering the national phase is available from WIPO's Internet site, via links from various pages of the site, including those of the *Gazette*, *Newsletter* and *Guide*, at http://www.wipo.int/pct/en/index.html.

Information about the requirements for **filing a demand for international preliminary examination** is set out in the *PCT Applicant's Guide*, Volume I/A, Chapter IX. Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 16 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before the date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 16-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 16-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau and if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances (Rule 17.1(c)).

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit (and all other PCT time limits) is the filing date of the earliest application whose priority is claimed (Article 2(xi)(b)).

Atty. Docket No.: 102782-201

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PATENT COOPERATION TREATY

In re Application of:	:	ARCH CHEMICALS, INC.
International Application No.	:	PCT/US2006/045645
Filed	:	29 NOVEMBER 2006
For	:	COATED CALCIUM HYPOCHLORITE COMPOSITION

Corresponding to United States
Provisional Application : 60/741,503 Filed: 01 DECEMBER 2005
Corresponding to United States
Patent Application : 11/602,816 Filed: 21 NOVEMBER 2006

CORRECTION OF DEFECTS IN THE INTERNATIONAL APPLICATION UNDER PCT ARTICLES 3(4)(i) and 14(1) and Rule 26

Mail Stop PCT
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Attention: RO/US

Dear Sir:

This is to correct a defect in the above-identified International Application. Specifically, Applicant encloses drawing sheets 1/2 to 2/2.

The Receiving Office is respectfully requested to substitute drawing sheets 1/3 to 3/3 currently filed in the application with replacement drawing sheet 1/2 to 2/2 presently enclosed.

Express Mail No. EV 614 567 614US

If the Receiving Office requires any additional information, the authorized Officer is invited to contact Applicant's Agent/Attorney at the telephone number listed below.

Respectfully submitted,

Enclosure

ARCH CHEMICALS, INC.

Date: 18 JAN 2007

Todd E. Garabedian

Todd E. Garabedian, Ph.D., Reg. No.: 39,197
Agent and Attorney for Applicant
Direct: (860) 297-3716
E-Mail: tgarabedian@wiggin.com

Wiggin and Dana LLP
One Century Tower
New Haven, CT 06508-1832
Tel. No. (203) 498-4400
Fax No. (203) 782-2889

\12800\629\632957.1

A MULTILAYER COATED CALCIUM HYPOCHLORITE

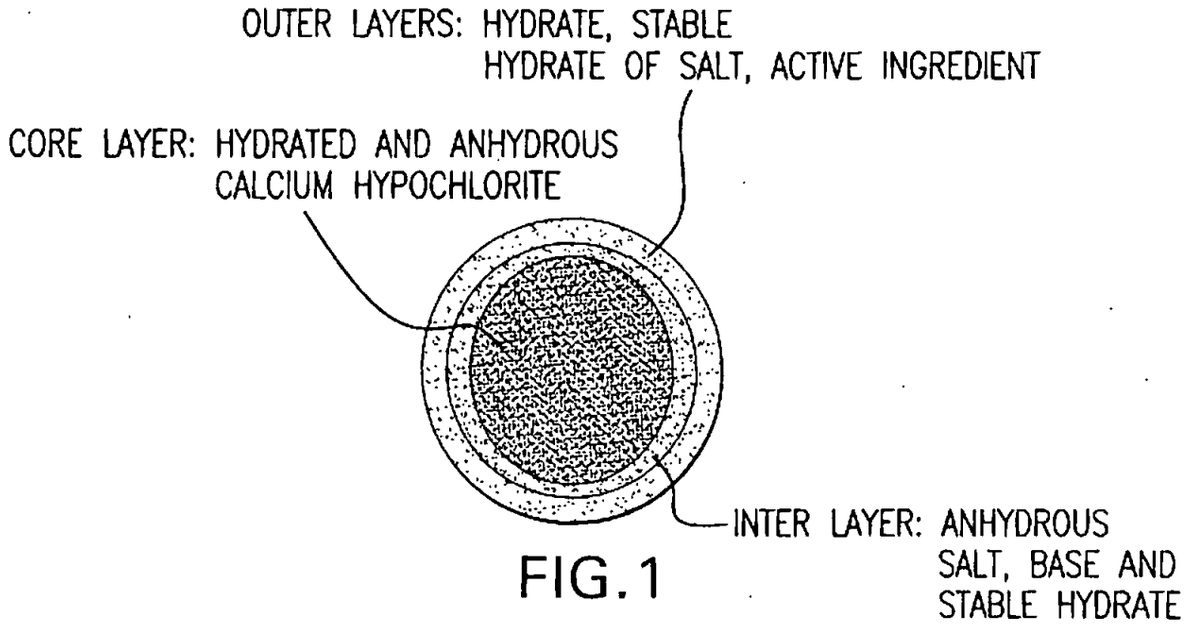


FIG.1

ELEMENTAL MAP ANALYSIS OF COATED SAMPLE 3

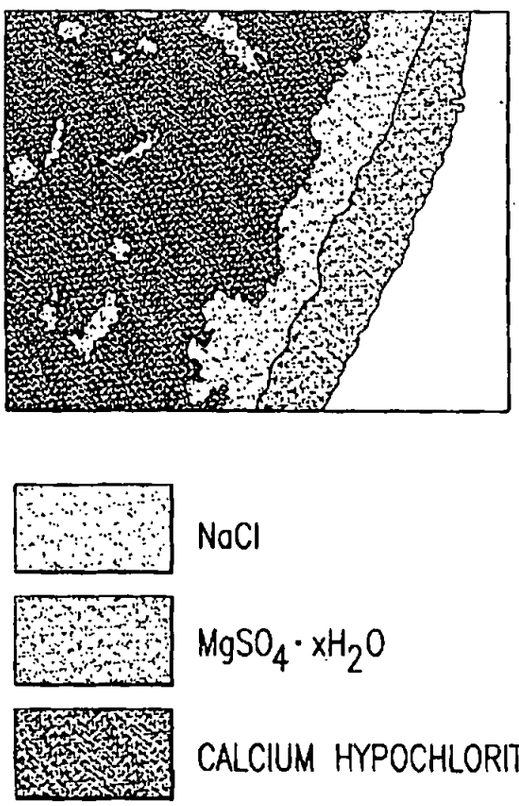
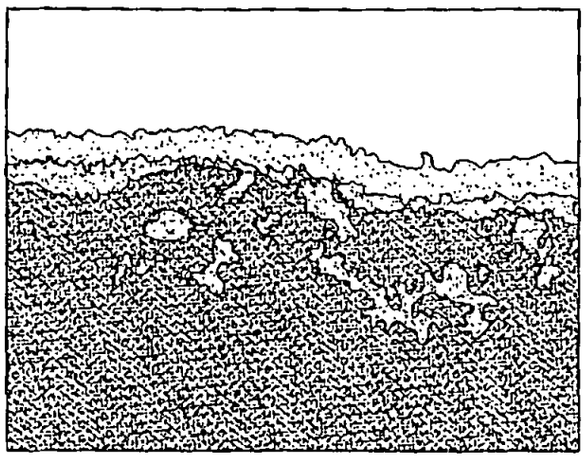


FIG.2

IMAGE OF THE COATED SAMPLE 16



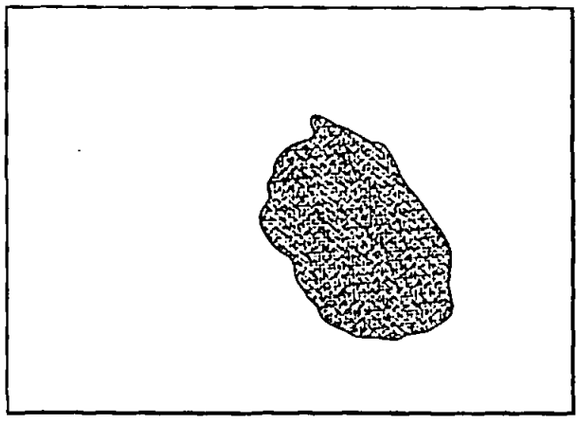
COPPER SULFATE·zH_2O

MAGNESIUM SULFATE·xH_2O

CALCIUM HYPOCHLORITE

FIG.3

ELEMENTAL MAP ANALYSIS
OF THE COATED SAMPLE 16



CALCIUM HYPOCHLORITE

FIG.4

Express Mail #EV 614 567 614US

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PATENT COOPERATION TREATY

In re Application of	:	ARCH CHEMICALS, INC.
International Application No.	:	PCT/US2006/045645
Filed	:	29 NOVEMBER 2006
For	:	COATED CALCIUM HYPOCHLORITE COMPOSITION

Corresponding to United States
Provisional Application : 60/741,503 Filed: 01 DECEMBER 2005
Corresponding to United States
Patent Application : 11/602,816 Filed: 21 NOVEMBER 2006

CORRECTION OF DEFECTS IN THE INTERNATIONAL APPLICATION UNDER PCT ARTICLES 3(4)(i) and 14(1) and Rule 26

Mail Stop PCT
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Attention: RO/US

Dear Sir:

In response to the Invitation to Correct Defects in the International Application (Form PCT/RO/106) mailed 12 January 2007 and having a statutory period for response set to expire on February 12, 2007, Applicant encloses the signed Power of Attorney from the Applicant, Arch Chemicals, Inc., which addresses the defects noted on Annex A1. to Form PCT/RO/106.

In the event that further correction of defects is required, the Authorized Officer is invited to contact Applicant's Agent/Attorney at the telephone number listed below.

Respectfully submitted,

Enclosure

ARCH CHEMICALS, INC.

Date: 18 JAN 2007

Todd E. Garabedian, Ph.D., Reg. No.: 39,197
Agent and Attorney for Applicant
Direct: (860) 297-3716
E-Mail: tgarabedian@wiggin.com

WIGGIN AND DANA LLP
ONE CENTURY TOWER
NEW HAVEN, CT 06508
Tel. No.: (203) 498-4400
Fax No.: (203) 782-2889

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PCT

POWER OF ATTORNEY

for an international application filed under the Patent Cooperation Treaty
(PCT Rule 90.4)

The undersigned applicant(s) (*Names should be indicated as they appear in the request*):

Arch Chemicals, Inc.
501 Merritt 7
P.O. Box 5204
Norwalk, Connecticut 06856-5204
United States of America
Telephone No.: 203-229-2900
Facsimile No.: 203-229-2613

hereby appoints (appoint) the following person as: [X] agent ☐ common representative

Name and address
(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

CARLSON, Dale Lynn; **DENTE**, Sherri; **GANGEMI**, Anthony P.; **GARABEDIAN**, Todd E.; **GALLETTA**, Elisabeth A.; **ROSENBLATT**, Gregory S.;
WIGGIN and DANA LLP, One Century Tower, New Haven, Connecticut 06508-1832
United States of America
Telephone No. 203-498-4400
Facsimile No. 203-782-2889

to represent the undersigned before [X] all the competent International Authorities

☐ the International Searching Authority only

☐ the International Preliminary Examining Authority only

in connection with the international application(s) identified below:

Title of Invention	Applicant's or Agent's File Reference	International Application Number (if already available)
COATED CALCIUM HYPOCHLORITE COMPOSITION	102782-201	

filed with the following Office, US, as Receiving Office and to make or receive payments on behalf of the undersigned.

Signature of the applicant(s) (*where there are several applicants, each of them must sign; next to each signature, indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading the request or this power*):

ARCH CHEMICALS, INC.

By: _____
Louis S. Massimo
Executive Vice President and Chief Financial Officer

Date: December 4, 2006

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PATENT COOPERATION TREATY

From the RECEIVING OFFICE

To:
TODD E. GARABEDIAN, PH.D.
WIGGIN AND DANA LLP
ONE CENTURY TOWER
NEW HAVEN, CONNECTICUT 06508-1832

RECEIVED
JAN 16 2007
By

PCT

INVITATION TO CORRECT DEFECTS IN THE INTERNATIONAL APPLICATION

(PCT Articles 3(4)(i) and 14(1) and Rule 26)

	Date of mailing *(day/month/year)* 12 Jan 2007
Applicant's or agent's file reference 102782-201	REPLY DUE within 1 months/days from the above date of mailing
International application No. PCT/US2006/045645	International filing date *(day/month/year)* 29 Nov 2006
Applicant ARCH CHEMICALS, INC.	

1. ☒ The applicant is hereby invited, within the time limit indicated above, to correct, in the international application as filed, the defects specified on the attached:
   - ☒ Annex A
   - ☐ Annex B1 *(text matter of the international application as filed)*
   - ☐ Annex C1 *(drawings of the international application as filed)*

2. ☐ The applicant is hereby invited, within the time limit indicated above, to correct, in the translation of the international application furnished under Rule 12.3 or 12.4, the defects specified on the attached:
   - ☐ Annex A
   - ☐ Annex B2 *(text matter of the translation of the international application)*
   - ☐ Annex C2 *(drawings of the translation of the international application)*

Additional observations (if necessary):

HOW TO CORRECT THE DEFECTS?

Correction must be submitted by filing a replacement sheet embodying the correction and a letter accompanying the replacement sheet, which shall draw attention to the difference between the replaced sheet and the replacement sheet. A correction may be stated in a letter only if it is of such a nature that it can be transferred from the letter to the record copy without adversely affecting the clarity and direct reproducibility of the sheet onto which the correction is to be transferred (Rule 26.4).

ATTENTION

Failure to correct the defects will result in the international application being considered withdrawn by this receiving Office (see Rule 26.5 for further details).

A copy of this invitation and any attachments has been sent to the International Bureau
- ☒ and the International Searching Authority

Name and mailing address of the receiving Office Mail Stop PCT, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450	Authorized officer Darlene Proctor dp
Facsimile No. 571-273-3201	Telephone No. 703-308-9290 EX 115

Form PCT/RO/106 (January 2004)

ANNEX A TO FORM PCT/RO/106

International application No.
PCT/US2006/045645

The receiving Office has found the following defects in the international application as filed:

1. As to **signature** of the international application (Rules 4.15, 26.2*bis*(a) and 90.4), the request:
   - a. ☐ is not signed* by the applicant or, if there is more than one applicant, by at least one of them
   - b. ☐ is not accompanied by the statement referred to in the check list in Box No. IX of the request explaining the lack of the signature of an applicant for the designation of the United States of America
   - c. ☒ is signed by what appears to be an agent/common representative but:
     - ☐ the international application is not accompanied by a power of attorney appointing him
     - ☒ the power of attorney accompanying the international application is not signed by all the applicants
   - d. ☐ other *(specify)*:

* Although Rule 4.15 requires that all applicants must sign the request (e.g. including all inventors/applicants for the designation of the United States of America), for the purposes of Article 14(1)(a)(i), if there is more than one applicant, it shall be sufficient that the request be signed by one of them (Rule 26.2*bis*(a))

However, the applicant's attention is drawn to the fact that the national law applied by each designated Office may require, in connection with the processing of the international application in the national phase, that the applicant furnish the confirmation of the international application by the signature of any applicant for the designated State who has not signed the request (Rule 51*bis*.1(a)(vi)).

2. As to indications concerning the **applicant*** who is entitled, according to Rule 19.1, to file the international application with the receiving Office, the request (Rules 4.4, 4.5 and 26.2*bis*(b)):
   - a. ☐ does not properly indicate the applicant's name *(specify)*:
   - b. ☐ does not indicate the applicant's address
   - c. ☐ does not properly indicate the applicant's address *(specify)*:
   - d. ☐ does not indicate the applicant's nationality
   - e. ☐ does not indicate the applicant's residence

☐ Further observations about indications concerning other applicants (if applicable):

* Although Rules 4.4 and 4.5 require indications concerning the applicant, or if there are several applicants, of each of them, for the purposes of Article 14(1)(a)(ii), if there is more than one applicant, it shall be sufficient that the indications required under Rule 4.5(a)(ii) and (iii) be provided in respect of one of them who is entitled according to Rule 19.1 to file the international application with the receiving Office (Rule 26.2*bis*(b)).

However, the applicant's attention is drawn to the fact that the national law applied by each designated Office may require, in connection with the processing of the international application in the national phase, that the applicant furnish any missing indication required under Rule 4.5(a)(ii) and (iii) in respect of any applicant for the designated State (Rule 51*bis*.1(a)(vii)).

3. As to the **language** of certain elements of the international application, other than the description and claims (Rules 12.1(c) and 26.3*ter*(a) and (c)):
   - a. ☐ the request is not in a language of publication accepted by this receiving Office, (the) language(s) accepted by this receiving Office is/are:
   - b. ☐ the text matter of the drawings is not in the language in which the international application is to be published, which is:
   - c. ☐ the abstract is not in the language in which the international application is to be published, which is:

4. The **title** of the invention:
   - a. ☐ is not indicated in Box No. I of the request (Rule 4.1(a))
   - b. ☐ is not indicated at the top of the first sheet of the description (Rule 5.1(a))
   - c. ☐ as appearing in Box No. I of the request is not identical with the title heading the description (Rule 5.1(a))

5. As to the **abstract** (Rules 8 and 26.1(b)):
   - ☐ the international application does not contain an abstract

PATENT COOPERATION TREATY

From the RECEIVING OFFICE

To:
TODD E. GARABEDIAN, PH.D.
WIGGIN AND DANA LLP
ONE CENTURY TOWER
NEW HAVEN, CONNECTICUT 06508-1832

RECEIVED
JAN 16 2007
By

PCT

NOTIFICATION OF THE INTERNATIONAL APPLICATION NUMBER AND OF THE INTERNATIONAL FILING DATE

(PCT Rule 20.5(c))

Date of mailing *(day/month/year)*	12 Jan 2007
Applicant's or agent's file reference: 102782-201	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2006/045645	29 Nov 2006	01 Dec 2005

Applicant: ARCH CHEMICALS, INC.

Title of the invention: COATED CALCIUM HYPOCHLORITE COMPOSITION

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.

2. The applicant is further notified that the record copy of the international application:

☒ was transmitted to the International Bureau on 12 Jan 2007

☐ has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau*:

☐ because the necessary national security clearance has not yet been obtained.

☐ because *(reason to be specified)*:

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

3. FOREIGN TRANSMITTAL LICENSE INFORMATION Completed by: OP

☐ Additional license for foreign transmittal not required. This subject matter is covered by a license already granted or the equivalent U.S. national application. Refer to that license for information concerning its scope.

☐ License for foreign transmittal not required 37 CFR 5.11(e)(1) or 37 CFR 5.11(c)(2). However, a license may be required for additional subject matter. See 37 CFR 5.15(h).

☒ Foreign transmittal license granted. 35 U.S.C. 184; 37 CFR 5.11 on 06 Jan 2007 (date)

☐ 37 CFR 5.15(a) ☒ 37 CFR 5.15(b)

Name and mailing address of the receiving Office	Authorized officer
Mail Stop PCT, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450	Darlene Proctor
Facsimile No. 571-273-3201	Telephone No. 703-308-9290 EX 115

Form PCT/RO/105 (July 1992)

PATENT COOPERATION TREATY

From the RECEIVING OFFICE

To:

TODD E. GARABEDIAN, PH.D.
WIGGIN AND DANA LLP
ONE CENTURY TOWER
NEW HAVEN, CONNECTICUT 06508-1832

PCT

COMMUNICATION IN CASES FOR WHICH NO OTHER FORM IS APPLICABLE

	Date of mailing *(day/month/year)*: 12 Jan 2007
Applicant's or agent's file reference: 102782-201	REPLY DUE: See paragraph 1 below
International application No.: PCT/US2006/045645	International filing date *(day/month/year)*: 29 Nov 2006
Applicant: ARCH CHEMICALS, INC.	

1. ☐ REPLY DUE within _____ months/days from the above date of mailing

☐ NO REPLY DUE, however, see below _____

☒ IMPORTANT COMMUNICATION

☐ INFORMATION ONLY

2. COMMUNICATION:

The applicant's attention is drawn to the fact that according to the national law of the United States of America, only the inventor is entitled to file a national application (Article 27(3)). The United States of America is designated in the international application, however, (i) The named inventor(s) is (are) not also indicated as applicant(s) for the purposes of the designation of the United States of America, and is (are) not indicated as being deceased; or (ii) no inventor is indicated.If no inventor is indicated as applicant for the purposes of the designation of the United States of America, the application may be rejected by the United States Patent and Trademark Office as a designated Office.

Name and mailing address of the receiving Office Mail Stop PCT, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-3201	Authorized officer Darlene Proctor dp Telephone No. 703-308-9290 EX 115

Form PCT/RO/132 (July 1992; reprint January 2004)

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To:

TODD E. GARABEDIAN, PH.D.
WIGGIN AND DANA LLP
ONE CENTURY TOWER
NEW HAVEN, CONNECTICUT 06508-1832

RECEIVED
JAN 16. 2007
By

PCT

NOTIFICATION OF RECEIPT OF SEARCH COPY

(PCT Rule 25.1)

Date of mailing *(day/month/year)*	12 Jan 2007
Applicant's or agent's file reference: 102782-201	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2006/045645	29 Nov 2006	01 Dec 2005

Applicant

ARCH CHEMICALS, INC.

1. **Where the International Searching Authority and the receiving Office are not the same Office:**
The applicant is hereby notified that the search copy of the international application was received by this International Searching Authority on the date indicated below.

Where the International Searching Authority and the receiving Office are the same Office:
The applicant is hereby notified that the search copy of the international application was received on the date indicated below.

12 Jan 2007 *(date of receipt).*

2. ☐ The search copy was accompanied by a nucleotide and/or amino acid sequence listing or tables related thereto in computer readable form.

3. **Time limit for establishment of international search report and written opinion of the International Searching Authority**
The applicant is informed that the time limit for establishing the international search report and the written opinion of the International Searching Authority is three months from the date of receipt indicated above or nine months from the priority date, whichever time limit expires later (Rules 42.1 and 43*bis*.1(a)).

4. A copy of this notification has been sent to the International Bureau and, where the first sentence of paragraph 1 applies, to the receiving Office.

Name and mailing address of the ISA/	Authorized officer
Mail Stop PCT, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450	Darlene Proctor dp
Facsimile No. 571-273-3201	Telephone No. 703-308-9290 EX 115

Form PCT/ISA/202 (January 2004)

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POWER OF ATTORNEY

for an international application filed under the Patent Cooperation Treaty
(PCT Rule 90.4)

The undersigned applicant(s) (*Names should be indicated as they appear in the request*):

Arch Chemicals, Inc.
501 Merritt 7
P.O. Box 5204
Norwalk, Connecticut 06856-5204
United States of America
Telephone No.: 203-229-2900
Facsimile No.: 203-229-2613

hereby appoints (appoint) the following person as: [X] agent ☐ common representative

Name and address
(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

CARLSON, Dale Lynn; **DENTE**, Sherri; **GANGEMI**, Anthony P.; **GARABEDIAN**, Todd E.; **GALLETTA**, Elisabeth A.; **ROSENBLATT**, Gregory S.;
WIGGIN and DANA LLP, One Century Tower, New Haven, Connecticut 06508-1832
United States of America
Telephone No. 203-498-4400
Facsimile No. 203-782-2889

to represent the undersigned before [X] all the competent International Authorities

☐ the International Searching Authority only

☐ the International Preliminary Examining Authority only

in connection with the international application(s) identified below:

Title of Invention	Applicant's or Agent's File Reference	International Application Number (if already available)
COATED CALCIUM HYPOCHLORITE COMPOSITION	102782-201	

filed with the following Office, US, as Receiving Office and to make or receive payments on behalf of the undersigned.

Signature of the applicant(s) (*where there are several applicants, each of them must sign; next to each signature, indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading the request or this power*):

ARCH CHEMICALS, INC.

By: _____
Louis S. Massimo
Executive Vice President and Chief Financial Officer

Date: _____, 2006

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)* 102782-201

Box No. I TITLE OF INVENTION

COATED CALCIUM HYPOCHLORITE COMPOSITION

Box No. II APPLICANT ☐ This person is also inventor

Name and address: *(Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

ARCH CHEMICALS, INC.
501 Merritt 7
P.O. Box 5204
Norwalk, Connecticut 06508-5204
United States of America

Telephone No. 203-229-2900

Facsimile No. 203-229-2613

Teleprinter No.

Applicant's registration No. with the Office

State *(that is, country)* of nationality: US

State *(that is, country)* of residence: US

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

LEI, Deqing
14 Eastgate Lane
Hamden, Connecticut 06514
United States of America

This person is:
☐ applicant only
☐ applicant and inventor
☒ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

GARABEDIAN, Ph.D., Todd E.
WIGGIN and DANA LLP
One Century Tower
New Haven, Connecticut 06508-1832
United States of America

Telephone No. 860-297-3716

Facsimile No. 203-782-2889

Teleprinter No.

Agent's registration No. with the Office 39,197

☐ **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

POLSON, George
8295 Old Woods Court
Springboro, Ohio 45066
United States of America

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☒ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

OBERSON, Sonia
44 Tower Lane
Shelton, Connecticut 06484
United States of America

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☒ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

MEYER, Ellen M.
3287 Chestnut Circle, NW
Cleveland, Tennessee 37312
United States of America

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☒ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

KILBY, James D.
928 Tri Circle NE
Cleveland, Tennessee 37312
United States of America

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☒ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No. V DESIGNATIONS

The filing of this request **constitutes under Rule 4.9(a), the designation** of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.

However,

- ☐ DE Germany **is not designated** for any kind of national protection
- ☐ JP Japan **is not designated** for any kind of national protection
- ☐ KR Republic of Korea **is not designated** for any kind of national protection
- ☐ RU Russian Federation **is not designated** for any kind of national protection

(The check-boxes above may only be used to exclude (irrevocably) the designations concerned if, at the time of filing, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application. See the Notes to Box No. V as to the consequences of such national law provisions in these States).

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application *(day/month/year)*	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1) 01 December 2005 (01.12.05)	60/741,503	US		
item (2) 21 November 2006 (21.11.06)	11/602,816	US		
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office)* identified above as:

☐ all items ☒ item (1) ☒ item (2) ☐ item (3) ☐ other, see Supplemental Box

* *Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):*

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):*

ISA / US

Request to use results of earlier search; reference to that search *(if an earlier search has been carried out by or requested from the International Searching Authority):*

Date *(day/month/year)*	Number	Country *(or regional Office)*
21 November 2006 (21.11.06)	11/602,816	US

Box No. VIII DECLARATIONS

The following **declarations** are contained in Boxes Nos. VIII (i) to (v) *(mark the applicable check-boxes below and indicate in the right column the number of each type of declaration)*:		Number of declarations
☐ Box No. VIII (i)	Declaration as to the identity of the inventor :	
☐ Box No. VIII (ii)	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent :	
☐ Box No. VIII (iii)	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application :	
☐ Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America) :	
☐ Box No. VIII (v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty :	

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Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:		Number of sheets
(a) on paper, the following number of sheets:		
request (including declaration sheets)	:	4
description (excluding sequence listing and/or tables related thereto)	:	23
claims	:	5
abstract	:	1
drawings	:	3
Sub-total number of sheets	:	36
sequence listing	:	
tables related thereto	:	
(for both, actual number of sheets if filed on paper, whether or not also filed in electronic form; see (c) below)		
Total number of sheets	:	36
(b) ☐ only in electronic form (Section 801(a)(i))		
(i) ☐ sequence listing		
(ii) ☐ tables related thereto		
(c) ☐ also in electronic form (Section 801(a)(ii))		
(i) ☐ sequence listing		
(ii) ☐ tables related thereto		
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the		
☐ sequence listing:		
☐ tables related thereto:		
(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)		

This international application is accompanied by the following item(s) *(mark the applicable check-boxes below and indicate in right column the number of each item)*:		Number of items
1. ☒ fee calculation sheet	:	1
2. ☒ original separate power of attorney	:	1
3. ☐ original general power of attorney	:	
4. ☐ copy of general power of attorney; reference number, if any:	:	
5. ☐ statement explaining lack of signature	:	
6. ☐ priority document(s) identified in Box No. VI as item(s):	:	
7. ☐ translation of international application into *(language)*:	:	
8. ☐ separate indications concerning deposited microorganism or other biological material	:	
9. ☐ sequence listing in electronic form *(indicate type and number of carriers)*		
(i) ☐ copy submitted for the purposes of international search under Rule 13*ter* only (and not as part of the international application)	:	
(ii) ☐ *(only where check-box (b)(i) or (c)(i) is marked in left column)* additional copies including, where applicable, the copy for the purposes of international search under Rule 13*ter*	:	
(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column	:	
10. ☐ tables in electronic form related to sequence listing *(indicate type and number of carriers)*		
(i) ☐ copy submitted for the purposes of international search under Section 802(b-*quater*) only (and not as part of the international application)	:	
(ii) ☐ *(only where check-box (b)(ii) or (c)(ii) is marked in left column)* additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-*quater*)	:	
(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column	:	
11. ☒ other *(specify)*: Transmittal Letter & Post Card	:	

Figure of the drawings which should accompany the abstract:	1	**Language of filing** of the international application:	English

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Todd E. Garabedian

Todd E. Garabedian, Ph.D., Reg. No. 39,197
Agent

For receiving Office use only

1. Date of actual receipt of the purported international application:	2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

Brigard & Castro
BOGOTA - COLOMBIA

PODER

Yo (nosotros) **ARCH CHEMICALS, INC.**

domiciliado(s) en 501 Merritt 7, P.O. Box 5204, Norwalk, Connecticut 06856-5204, Estados Unidos de América

Nombro(amos) a: **JUAN PABLO CADENA SARMIENTO** y/o **BEATRIZ JARAMILLO** y/o **CARLOS H. PALACIO EASTMAN** y/o **HECTOR GOMEZ MEJIA**, de Bogotá, Colombia, apoderados verdaderos y legales con poder especial, amplio y suficiente, para recabar de las oficinas y autoridades colombianas administrativas, judiciales y de policía, en cualquier instancia o recurso, la obtención de patentes de invención, registros de marcas, diseños industriales, modelos de utilidad, depósitos de nombres comerciales y enseñas, registros de derechos de autor y contratos sobre los mismos, obtención de certificados de obtentor de variedades vegetales, así como sus prórrogas, renovaciones, anotaciones de traspaso, cambios de nombre y/o domicilio; elaborar, tramitar y registrar contratos de licencia y licencias de cualesquiera clases; intervenir como demandante o como demandado en cualquier instancia y recurso ante cualquier juez, corporación, funcionario público o autoridad en acciones judiciales, administrativas y de policía tales como: oposiciones al registro de marcas; acciones de caducidad, cancelación y nulidad; acciones reivindicatorias, acciones derivadas de la obtención o explotación de licencias; acciones de competencia desleal; demandas penales; acciones de indemnización de perjuicios, reclamos y observaciones a solicitudes de patentes, diseños industriales, modelos de utilidad, en el ejercicio de medidas cautelares y en otras acciones o medidas similares.

A este efecto, lo(s) faculto(amos) para elevar solicitudes, formular descripciones, enmiendas, protestas, declaraciones, oposiciones, cancelaciones, nulidades, apelaciones y reclamos; pagar impuestos, cuotas y gravámenes prescritos por la ley; renunciar o desistir a derechos concedidos o en curso de concesión; recibir toda clase de documentos y valores, dando el descargo respectivo, y, en general, para dar ante dichas autoridades todos los pasos necesarios al efecto indicado y tomar todas las medidas que creyeren conducentes al resguardo de mis (nuestros intereses), con todas las demás facultades legales necesarias.

Este poder comprende la facultad de ratificar o confirmar en mi (nuestro) nombre lo actuado así como la facultad de desistir, transigir, comprometer, y la de sustituirlo en todo o en parte y revocar sustituciones. Asimismo nombro(amos) a: **JUAN PABLO CADENA SARMIENTO** y/o **BEATRIZ JARAMILLO** y/o **CARLOS H. PALACIO EASTMAN** y/o **HECTOR GOMEZ MEJIA**, domiciliado(s) en la Carrera 7 No. 16-56 Piso 9, mis (nuestros) apoderados en Colombia, con facultades para recibir notificaciones y designar apoderados judiciales o extrajudiciales.

Otorgado y firmado en

hoy de de 200_

Firma

Nombre
Cargo

POWER OF ATTORNEY

I (We) **ARCH CHEMICALS, INC.**,

domiciled in 501 Merritt 7, P.O. Box 5204, Norwalk, Connecticut 06856-5204, United States of America.

Hereby appoints **JUAN PABLO CADENA SARMIENTO** and/or **BEATRIZ JARAMILLO** and/or **CARLOS H. PALACIO EASTMAN** and/or **HECTOR GOMEZ MEJIA**, of Bogotá, Colombia, my (our) true and lawful attorneys with special, ample and sufficient power to obtain from the Colombian administrative, judicial and police offices and authorities, in any instance, privileges of patents of invention, registration of trademarks, industrial designs and utility models; registration of commercial names and emblems, registration of copyright and contracts related thereto, certificates of obtainers of vegetables varieties, as well as extensions, renewals and recordal of assignments and changes of name and domicile related to the above; to prepare, prosecute and register licenses of any kind; to act as plaintiff or defendant in any instance or recourse, and before any judge, corporation, public official or authority in judicial, administrative and police actions, such as: oppositions to the registration of trademarks; caducity, cancellation and nullity actions; claim actions derived from the obtaining or exploitation of licenses, action of unfair competition; criminal proceedings, actions for payment of damages; claims or observations on patent applications, models, industrial designs and utility models; in the exercise of preventive measures and in other actions or similar proceedings.

To that effect they hereby empowered to file applications, formulate descriptions, amendments, protests, declarations, oppositions, cancellations, nullities, appeals and claims; to pay taxes, quotas and assessments prescribed by law, renounce or waive the rights granted or in the process of granting; to receive all kinds of documents and valuables, giving the respective release of receipt, and, in general, to take before said authorities the necessary steps to such effect, and any measures that they may deem pertinent to the safeguard of my (our) interest(s) with all the other necessary legal powers.

This power includes the faculty to ratify or confirm desist, settle and compromise on my (our) behalf, and to substitute this power in whole or in part and to revoke substitutions. At the same time I (We) hereby appoints **JUAN PABLO CADENA SARMIENTO** and/or **BEATRIZ JARAMILLO** and/or **CARLOS H. PALACIO EASTMAN** and/or **HECTOR GOMEZ MEJIA**, domiciled in Carrera 7 No. 16-56, Piso 9, my (our) attorney(s) in fact, with powers to receive notifications and to designate judicial and extrajudicial attorneys.

Granted and signed in Norwalk, Connecticut, U.S.A.

this 4 day Oct of 2005

ARCH CHEMICALS, INC.

Signature Paul J. Craney

Name Paul J. Craney
Title Executive Vice President

COMO FUNCIONARIO CONSULAR DE COLOMBIA CERTIFICO QUE LA FOTOCOPIA QUE ME PRESENTO ES FIEL COPIA DEL ORIGINAL
13 ABR. 2007
ROSA FALLA LASSO
NOTARIO CUARENTA Y SEIS ENCARGADO

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APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: The United States of America

THIS PUBLIC DOCUMENT

2. has been signed by **NANCY O. STEVENS**

3. acting in the capacity of **NOTARY PUBLIC**

4. in the State of Connecticut for the term of **June 21, 2001 to June 30, 2006**

CERTIFIED

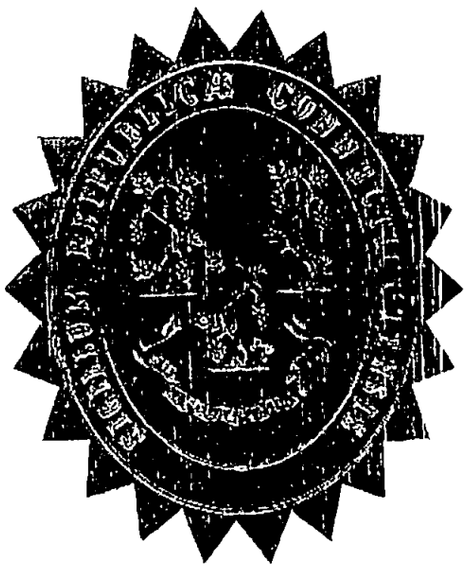
5. at Hartford, Connecticut

6. on **October 13, 2005**

7. by **SUSAN BYSIEWICZ** Secretary of the State of Connecticut

8. Number : **2005-12690**

9. Seal :



10. Signature

Secretary of the State

COLOMBIA

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I PAUL J. CRANEY Certify:

That ARCH CHEMICALS, INC.
is a Corporation duly organized and legally existing under the laws of the Commowealth of Virginia, U.S.A.

That the domicile of said Corporation
is 501 Merritt 7
P.O. Box 5204
Norwalk, Connecticut 06856-5204
U.S.A.

I, further certify that I am duly authorized to sign the forgoing instrument in the name of said corporation and that the purposes for which said instrument is granted are within the scope of the objects or activities of said corporation, in accordance with the Articles of Amendment & Restatement of the Articles of Incorporation, issued in the City of Richmond, Virginia, U.S.A. and filed February 3, 1999.

Signed in Norwalk, Connecticut, U.S.A.
Dated: 4 Oct, 2005

Paul J Craney
Paul J. Craney
Executive Vice President

STATE OF CONNECTICUT)
)
COUNTY OF FAIRFIELD)

On this 4th day October, 2005, before me a Notary Public in and for said County and State, personally appeared PAUL J. CRANEY, who acknowledged himself to be the Executive Vice President of ARCH CHEMICALS, INC., and that he as such Executive Vice President, being authorized so to do, executed the foregoing instrument for the purposes therein contained, by signing the name of the corporation by himself as Executive Vice President.

In witness whereof I hereunto set my hand.

Nancy O. Stevens
Notary Public

Seal:

My Commission Expires: June 30, 2006

13 ABR. 2007
ROSA FALLA LABBECA
NOTARIO CUARENTA Y SEIS ENCARGADO

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TRADUCCION AL ESPAÑOL del Documento de Poder otorgado por ARCH CHEMICALS, INC. domiciliada en 501 Merritt 7, Norwalk, Connecticut, Estados Unidos de América.

APOSTILLA

(Convención de La Haya del 5 de Octubre de 1961)

1. País: Estados Unidos de América

ESTE DOCUMENTO PUBLICO

2. ha sido firmado por **NANCY O. STEVENS**
3. actuando en capacidad de **NOTARIO PUBLICO**
4. en el Estado de Connecticut por el término de **junio 21 de 2001 a junio 30 de 2006**

CERTIFICADO

5. en Hartford, Connecticut
6. en **octubre 6 de 2005**
7. por **SUSAN BYSIEWICZ**, Secretaria del Estado de Connecticut
8. Número: **2005-12690**
9. Sello:

10. Firma

(Firma)

Secretario de Estado

COMO NOTARIO CUARENTA Y SEIS ENCARGADO DEL CIRCULO DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA CONCUERDA CON EL ORIGINAL QUE ME FUE PUESTO A LA VISTA EN BOGOTA D.C. REPUBLICA DE COLOMBIA

13 ABR. 2007

ROSA FALLA LAISECA
NOTARIO CUARENTA Y SEIS ENCARGADO

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Yo, PAUL J. CRANEY certifico:

Que ARCH CHEMICALS, INC.
Es una corporación debidamente organizada y legalmente existente bajo las leyes de la Mancomunidad de Virginia, Estados Unidos de América.

Que el domicilio de dicha corporación
es 501 Merritt 7
Casilla Postal 5204
Norwalk, Connecticut 06856-5204
Estados Unidos de América

Certifico además que estoy debidamente autorizado para firmar el documento anterior en nombre de dicha corporación y que los propósitos para los cuales se concede dicho documento están dentro del alcance de los objetos o actividades de dicha corporación, de acuerdo con los Artículos de Enmienda & Restablecimiento de los Artículos de Incorporación, emitidos en la ciudad de Richmond, Virginia, Estados Unidos de América y presentados el 3 de febrero de 1999.

Firmado en Norwalk, Connecticut, Estados Unidos de América
Fechado: 4 de octubre de 2005

(Firma)
Paul J. Craney
Vicepresidente Ejecutivo.

ESTADO DE CONNECTICUT)
)
CONDADO DE FAIRFIELD)

Este 4 de octubre de 2005, ante mí un Notario Público en y para dicho Condado y Estado, personalmente apareció PAUL J. CRANEY, quien reconoció ser el Vicepresidente Ejecutivo de ARCH CHEMICALS, INC., y que él como tal Vicepresidente Ejecutivo, estando autorizado ara hacerlo, ejecutó el instrumento anterior para los propósitos allí contenidos, firmando a nombre de la corporación por si mismo como Vicepresidente Ejecutivo.

En testimonio de lo cual he puesto mi firma

(Firma)
Notario Público

Sello: Mi comisión expira: Junio 30 de 2006