

Señores
DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Bogotá, D.C.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Rad: 05-128098-00003-0000
Fee: 2005-07-25 10:38:21 Dep. 2020 NUECREACIONES
Tra. 11 PATENTE/YS
Ene. 379 FASENACIONALI
Act. 329 CTOINFORMACION Folios: 83

Re.: Código 011-379-444
Expediente No. 05-128.098
Fase Nacional de Solicitud
de Patente PCT
COATING SYSTEMS LABORATORIES,
INC. y NORTHERN FILTER MEDIA, INC.

En relación con el expediente de la referencia y dando cumplimiento a la última providencia recaída sobre este asunto por medio del presente escrito me permito manifestarles lo siguiente:

1. La sociedad NORTHERN GRAVEL COMPANY cambió su nombre a NORTHERN FILTER MEDIA, INC. por lo cual se adjunta el formulario de modificación de la solicitud.
2. Acompaño copias auténticas de los poderes conferidos por las sociedades solicitantes, debidamente legalizados con sus correspondientes sustituciones a favor del suscrito.
3. Debido a que la solicitud estadounidense No. 60/472,429 de la cual se reivindica prioridad es una solicitud provisional y en los Estados Unidos no se requiere documento de traspaso de los inventores para este tipo de solicitud adjunto los documentos de que acreditan el traspaso de los inventores en relación con la solicitud de patente estadounidense No.

10/850,121 que a su vez reivindica la prioridad de la solicitud provisional No. 60/472,429, al igual que una copia certificada de la solicitud de patente No. 10/850,121.

4. Adjunto el formulario de solicitud con la fecha de la solicitud PCT/US2004/15853 corregida.
5. El Examen Preliminar Internacional no se encuentra disponible a la fecha por lo cual no es posible anexarlo ni anexar la traducción correspondiente.
6. Se acompaña el comprobante de pago por concepto de modificación de la solicitud recibo No. 06-56,227

Renuncio al término faltante de traslado, y les solicito ordenar la publicación del extracto.

De Ustedes Atentamente,


LUIS FELIPE CASTILLO GIBSONE
T.P. No. 68.995 del C.S.J.

FORMULARIO ÚNICO DE CORRECCIONES Y MODIFICACIONES
2000-10

1

SOLICITUD DE:

☐

Corrección de Error Material

☒

Modificación a una Solicitud.

2

SOLICITANTE

Nombre: COATING SYSTEMS LABORATORIES,
INC. y NORTHERN FILTER MEDIA, INC.

Dirección: 221 East Chilton Drive y
Pettibone Avenue

Teléfono:

E-mail

Domicilio Chandel, Arizona y Muscatine, Iowa
(E.U.A.)

IDENTIFICACIÓN

C.C. ☐

NIT

☐

C.E. ☐

Otro

☐

Número _____

3

REPRESENTANTE
O APODERADO

Nombre: LUIS FELIPE CASTILLO GIBSONE

Dirección: Carrera 13 No. 37-43 Piso 12

Teléfono: 285 74 60

Fax: 285 92 67

E-mail info@castillograu.com

IDENTIFICACIÓN

C.C. ☒

NIT

☐

C.E. ☐

Otro

☐

Número 79.397.879 T.P. 68.995
de Bogotá del

4

Número de Expediente

05-128.098

5

Descripción de la corrección o modificación solicitada

Cambio de Nombre de la solicitante

NORTHERN GRAVEL COMPANY a NORTHERN FILTER MEDIA, INC.

6

Comprobante de pago N°

06-56, 227

Fecha

25/07/006

7

Anexos:

☒

Comprobante de pago de la tasa

☒

Poderes, si fuere el caso

☒

Certificado de existencia y representación legal de las partes, cuando sean personas jurídicas.

8

NOMBRE LUIS FELIPE CASTILLO GIBSONE

FIRMA



C.C. 79.397.879 de Bogotá T.P. 68.995 del
C.S.J.

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

*47

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Rad: 05-128088-00003-0000
Pec: 2006-07-25 10:38:21 Dep. 2000 NUECREACIONES
Tel. 11 PATENTERYII
Ext: 379 FASENACIONALI
Art 329 CTORINFORMACION Folios: 63

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 06 - 56,227
FECHA : JULIO 25 DE 2006

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CASTILLO GRAU Y ASOCIADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	53786744	25/07/2006	525,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03	CAMBIO DE MODALIDAD Y MODIFICA	
12		MARCAS Y LEYAS COMERCIALES	95,000.00
		TOTAL :	95,000.00

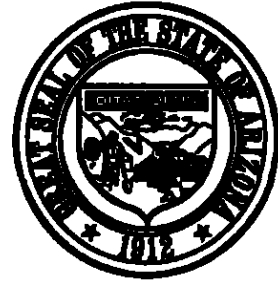
SON: NOVENTA Y CINCO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ARIZONA

Department of State



48

APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

This public document

2. has been signed by CANDIS ANN STRUCK

3. acting in the capacity of Notary Public

4. bears the seal/stamp of CANDIS ANN STRUCK - Notary Public

CERTIFIED

5. at Phoenix, Arizona

6. on Thursday, March 23, 2006

7. by the Secretary of State, State of Arizona

8. No. 158671

9. Seal / stamp

10. Signature

Como Notario Venticinco del Circuito de Bogotá, hago constar que esta copia coincide con original que se ha presentado Bogotá D.C. - Colombia.

21 JUN 2006

GUSTAVO SAMPER RODRIGUEZ
NOTARIO VENTICINCO

Jahice K. Brewer

Jahice K. Brewer
Secretary of State

FOR PATENTS AND TRADE MARKS IN

COLOMBIA

PODER GENERAL

GENERAL POWER OF ATTORNEY

(1) COATING SYSTEMS
LABORATORIES, INC.

(1) COATING SYSTEMS
LABORATORIES, INC.

1 Applicant's name

domiciliado en (2) 211 East Chilton
Drive, Chandler, Arizona
85076-0386, EUA

domiciled in (2) 211 East Chilton
Drive, Chandler, Arizona
85076-0386, USA,

2 Applicant's Address

nombró al Dr. (3) German Castillo Grau y/o Adriana
Castillo Gibson y/o Luis Felipe Castillo Gibson...

hereby appoint Dr. (3) German Castillo Grau and/or
Adriana Castillo Gibson and/or Luis Felipe Castillo
Gibson...

E d A

3 Leave blank

... con oficinas en la
Carrera 13 No. 37 -43 Piso 12 en Bogotá,
Colombia como sus representantes con poder
especial amplio y suficiente, para recibir de
las oficinas y autoridades Colombianas,
administrativas, judiciales o de policía, en
primera o segunda instancia, la obtención de
Patentes de Invención, Registro de Marcas, de
Modelos y de Dibujos Industriales, de Nombres
Comerciales y Enseñas, lo mismo que
traspasos, extensiones, renovaciones, cambios
de nombre, registro de licencias de explotación
y registro de licencias de uso referentes a tales
actuaciones, a cuyo efecto les faculta para dar
ante dichas autoridades todos los pasos
necesarios al objeto indicado, elevar
solicitudes, formular descripciones, enmiendas,
protestas, declaraciones, apelaciones y
reclamos, solicitar la aplicación de medidas
cautelares, aceptar en nuestro nombre y
representación la Cesión de derechos de
Invención y de patente de Invención que se nos
haga por cualquier persona, abonar todos los
impuestos, cuotas y pagos determinados por la
ley, recibir todos los documentos y valores
dando el descargo respectivo, llenar
cualesquiera otros requisitos, desistir y tomar
en fin todas las medidas que creyeran
conducentes al resguardo de nuestros
intereses y en caso de presentarse oposiciones
para que intervengan como demandantes o
como demandados, con todas las demás
facultades legales necesarias. Este poder
comprende además las facultades de recibir,
desistir, transigir, comprometer, sustituir,
revocar sustituciones, recibir notificaciones y
nombrar apoderados judiciales o extra-
judiciales.

With
offices at Carrera 13 No. 37 -43 Piso 12 en
Bogotá, Colombia as our representatives with
special, ample and sufficient power to obtain
from the offices and Colombian authorities,
administrative, judicial and police, in first or in
second instance, Patents of Invention,
registration of trade Marks, of Models and
Industrial Drawings, of Commercial Names and
ensigns, as well as assignments, extensions,
renewals, changes of name, registration of
licences of exploitation and of licences of use
referring to said actions who are empowered to
take before said authorities all of the necessary
steps for the purposes indicated, to file
applications, to formulate descriptions,
corrections, protests, declarations, appeals and
claims, apply for precautionary measures, to
accept on our behalf and representation the
assignment of rights of invention and titles of
invention that may be done to us by any
person, to pay all taxes, quotas and payments
prescribed by law, to receive all the documents
and proceeds giving the respective acquittance
or receipt, to fulfill any other requisites to desist
and take in fact any other measures that may
be deemed conducive to the safeguard of our
interests, and in case oppositions are
presented to intervene as complainant and
defendant, with all necessary legal faculties.
This power of attorney includes the faculties to
receive, desist, compromise, transact,
substitute it in all or in part, to revoke
substitutions, to receive notifications and to
appoint extra-judicial or judicial attorneys.

4 Date

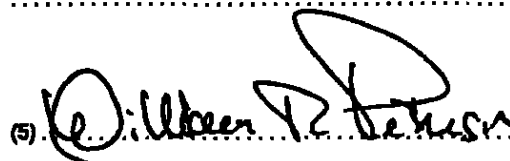
5 Applicant's signature

The applicant's signature
must be attested by a No-
tary Public through the
NOTARIAL CERTIFICATE:
In the "(Individual)", when
the signer is a natural
person; and in the
"(Corporations)", when is a
legal one. The Notary's
signature must then be
legalized by a Colombian
Consular Officer.

La firma del solicitante
debe ser atestada por un
Notario Público por medio
de la DECLARACION
NOTARIAL: en la "(Indivi-
dual)", cuando el firmante
es una persona natural; y
en la de "(Sociedades)",
cuando es una persona
jurídica. La firma del
notario deberá ser lega-
lizada por el Consulado
Colombiano.

Dado y firmado en (4) . Febrero. 28 . 2006...

Given and signed in (4) 2/28/06

(5) 

Corporate Seal to be affixed

Como Notario Venticinco del Circuito de
Bogotá, hago constar que esta copia
coincide con original que se ha presentado
Bogotá D.C. - Colombia.
21 JUN 2006
GUSTAVO SAMPER RODRIGUEZ
NOTARIO VENTISEIS

La declaración Notarial a la vuelta.
Notarial acknowledgement on other side.

DECLARACION NOTARIAL

(Individual)

A los días del mes de 19
comparecí personalmente ante mí, No-
tario Público

a quien(es) doy fé de conocer y me consta que
es (son) la(s) persona(s) descritas y fir-
mante(s) del documento que precede, decla-
rando ante mí que otorga(n) el mismo para los
fines y propósitos que en él se expresan.

El Notario Público,

NOTARIAL CERTIFICATE

(Individual)

On this day of 2006 personally
appeared before me, a Notary Public

...William R. Peterson...
to me known, and known to me be the
person(s) described in and who executed the
foregoing document, and he (they) duly ack-
nowledged to me that he (they) executed same
for the uses and purposes therein expressed.

Notary Public

(Sociedades)

El infrascrito Notario Certifica: que la firma
que antecede y dice
WILLIAM R. PETERSON

es auténtica; que el signatario desempeña
actualmente el cargo de PRESIDENTE

de COATING SYSTEMS LABOR-
ATORIES, INC.

que tiene facultad para otorgar este poder; y
que dicha compañía está domiciliada en
CHANDLER, ARIZONA, E. U. A.

y actualmete existe y está organizada de
acuerdo a las leyes de EL ESTADO
DE ARIZONA

Todos los hechos anteriores le constan por
haber examinado los documentos respectivos
y de todo ello da fé.

Dado y firmado en
.....

(Corporations)

The undersigned Notary Public certifies; that
the preceding signature reading
William R. Peterson

is authentic; that the signor at present fills the
post of President and Chief
Executive Officer

of Coating Systems Laboratories,
Inc.

and that he is empowered to grant this power;
and that said company is domiciled in
Chandler, Arizona, USA

and actually exists and is organized in accor-
dance with the laws of Arizona

all the foregoing facts are known to the No-
tary due to his having examined the respetive
documents to which he, the Notary attests

Granted and signed in GUSTAVO A. Z.
.....

El Notario Público

Como Notario Venticésimo del Circuito de
Bogotá, hago constar que esta copia
coincide con original que se ha presentado
Bogotá D.C. - Colombia.

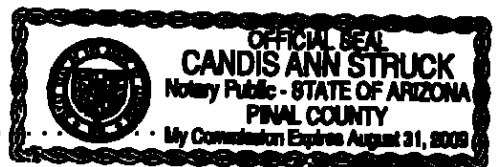
21 JUN. 2006

GUSTAVO SAMPER RODRIGUEZ

NOTARIO VENTISEIS

(Con legalización Consular)

Notary Public



June 05, 2006

IOWA

SECRETARY OF STATE

NORTHERN FILTER MEDIA, INC.

2509 PETTIBONE AVENUE
MUSCATINE, IA 52761 USA

APOSTILLE
(Convention de La Hague du 5 octobre 1961)

- 1 Country: United States of America
- 2 This public document has been signed by: DEBRA A SHELANGOSKI
- 3 Acting in the capacity of: NOTARY PUBLIC
- 4 Bearing the seal/stamp: NOTARY PUBLIC IN AND FOR THE STATE OF IOWA

CERTIFIED

- 5 at: DES MOINES, IOWA, UNITED STATES OF AMERICA.
- 6 date: MAY 30, 2006
- 7 by: the Secretary of State of the State of Iowa, United States of America
- 8 No. 06-043048
- 9 Seal

10 Signature

Como Notario Verificado del Circuito de Bogotá, hago constar que esta copia coincide con el original que se ha presentado Bogotá D.C. - Colombia.

21 JUN 2006

GUSTAVO SAMPER RODRIGUEZ
NOTARIO VEINTISEIS



Chester J. Culver
CHESTER J. CULVER SECRETARY OF STATE



FOR PATENTS AND TRADE MARKS IN

COLOMBIA

PODER GENERAL

GENERAL POWER OF ATTORNEY

(1). NORTHERN FILTER MEDIA, INC.

(1). NORTHERN FILTER MEDIA, INC

1 Applicant's name

domiciliado en (2) 2509 Pettibone
Avenue, Muscatine, Iowa
52761, BIA.

domiciled in (2) 2509 Pettibone
Avenue, Muscatine, Iowa
52761, USA.

2 Applicant's Address

nombre al Dr. (3) German Castillo Grau y/o Adriana
Castillo Gibeone y/o Luis Felipe Castillo Gibeone.

hereby appoint-Dr. (3) German Castillo Grau and/or
Adriana Castillo Gibeone and/or Luis Felipe Castillo
Gibeone

3 Leave blank

con oficinas en la Carrera 13 No. 37 -43 Piso 12 en Bogotá, Colombia como sus representantes con poder especial amplio y suficiente, para recabar de las oficinas y autoridades Colombianas, administrativas, judiciales o de policía, en primera o segunda instancia, la obtención de Patentes de Invención, Registro de Marcas, de Modelos y de Dibujos Industriales, de Nombres Comerciales y Enseñas, lo mismo que traspaños, extensiones, renovaciones, cambios de nombre, registro de licencias de explotación y registro de licencias de uso referentes a tales actuaciones, a cuyo efecto les faculta para dar ante dichas autoridades todos los pasos necesarios al objeto indicado, elevar solicitudes, formular descripciones, enmiendas, protestas, declaraciones, apelaciones y reclamos, solicitar la aplicación de medidas cautelares, aceptar en nuestro nombre y representación la Cesión de derechos de invención y de patente de invención que se nos haga por cualquier persona, abonar todos los impuestos, cuotas y pagos determinados por la ley, recibir todos los documentos y valores dando el descargo respectivo, llenar cualesquiera otros requisitos, desistír y tomar en fin todas las medidas que creyeren conducentes al resguardo de nuestros intereses y en caso de presentarse oposiciones para que intervengan como demandantes o como demandados, con todas las demás facultades legales necesarias. Este poder comprende además las facultades de recibir, desistír, transigir, comprometer, sustituir, revocar sustituciones, recibir notificaciones y nombrar apoderados judiciales o extra-judiciales.

With offices at Carrera 13 No. 37 -43 Piso 12 en Bogotá, Colombia as our representatives with special, ample and sufficient power to obtain from the offices and Colombian authorities, administrative, judicial and police, in first or in second instance, Patents of Invention, registration of trade Marks, of Models and Industrial Drawings, of Commercial Names and ensigns, as well as assignments, extensions, renewals, changes of name, registration of licences of exploitation and of licences of use referring to said actions who are empowered to take before said authorities all of the necessary steps for the purposes indicated, to file applications, to formulate descriptions, corrections, protests, declarations, appeals and claims, apply for precautionary measures, to accept on our behalf and representation the assignment of rights of invention and titles of invention that may be done to us by any person, to pay all taxes, quotas and payments prescribed by law, to receive all the documents and proceeds giving the respective acquittance or receipt, to fulfill any other requisites to desist and take in fact any other measures that may be deemed conducive to the safeguard of our interests, and in case oppositions are presented to intervene as complainant and defendant, with all necessary legal faculties. This power of attorney includes the faculties to receive, desist, compromise, transact, substitute it in all or in part, to revoke substitutions, to receive notifications and to appoint extra-judicial or judicial attorneys.

4 Date

5 Applicant's signature

The applicant's signature must be attested by a Notary Public through the NOTARIAL CERTIFICATE in the "(Individual)", when the signer is a natural person; and in the "(Corporations)", when is a legal one. The Notary's signature must then be legalized by a Colombian Consular Officer.

La firma del solicitante debe ser atestada por un Notario Público por medio de la DECLARACION NOTARIAL en el "(Individual)", cuando el firmante es una persona natural, y en la de "(Sociedades)", cuando es una persona jurídica. La firma del notario deberá ser legalizada por el Consulado Colombiano.

Dado y firmado en (4)

Como Notario Verificador del Circuito de Bogotá, hago constar que esta copia coincide con original que se ha presentado Bogotá D.C. Colombia.

Given and signed in (4)

22 JUN 2006

GUSTAVO SAMPER RODRIGUEZ
5/30/06 VENTISERS

(5) David P. Reussing
President

Corporate Seal to be affixed

La declaración Notarial a la vuelta.
Notarial acknowledgement on other side.

DECLARACION NOTARIAL

(Individual)

A los. . . . días del mes. de 19. . . .
comparecí. . . . personalmente ante mí, No-
tario Público.

a quien(es) doy fé de conocer y me consta que
es (son) la(s) persona(s) descritas y fir-
mante(s) del documento que precede, decia-
rando ante mí que otorga(n) el mismo para los
fines y propósitos que en él se expresan.

El Notario Público,

NOTARIAL CERTIFICATE

(Individual)

On this. day of. 19. . . . personally
appeared before me, a Notary Public

to me known, and known to me be the
person(s) described in and who executed the
foregoing document, and he (they) duly ack-
nowledged to me that he (they) executed same
for the uses and purposes therein expressed.

Notary Public

(Sociedades)

El infrascrito Notario Certifica: que la firma
que antecede y dice.

DAVID F. REUSSORG.

es auténtica; que el signatario desempeña
actualmente el cargo de PRESIDENTE

de HORTHERU FILTER
MEDIA INC.

que tiene facultad para otorgar este poder; y
que dicha compañía está domiciliada en . . .

MUSCATINE, IOWA, E. U. A.

y actualmete existe y está organizada de
acuerdo a las leyes de EL ESTADO . . .

DE IOWA

Todos los hechos anteriores le constan por
haber examinado los documentos respectivos
y de todo ello da fé.

Dado y firmado en

El Notario Público

(Corporations)

The undersigned Notary Public certifies; that
the preceding signature reading

is authentic; that the signor at present fills the
post of

of

and that he is empowered to grant this power;
and that said company is domiciled in

and actually exists and is organized in accor-
dance with the laws of

all the foregoing facts are known to the No-
tary due to his having examined the respetive
documents to which he, the Notary attests

Given and signed in

Como Notario Veintiseis del Circuito de
Bogotá, hego constar que esta copia
coincide con original que se ha ratificado
Bogotá D.C. - Colombia.
22 JUN 2006
GUSTAVO SAMPER RODRIGUEZ
NOTARIO VEINTISEIS

DEBRA A. SHELARGOSKI
Commission Number 716327
My Commission Expires
5/30/08

Debra A. Shelargoski
5/30/06

(Con legalización Consular)

(With Consular legalization)

Señores
DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Bogotá, D.C.

Re.: Expediente No. 05-128.098
Fase Nacional de Solicitud
de Patente PCT
COATING SYSTEMS LABORATORIES,
INC. y NORTHERN FILTER MEDIA, INC.

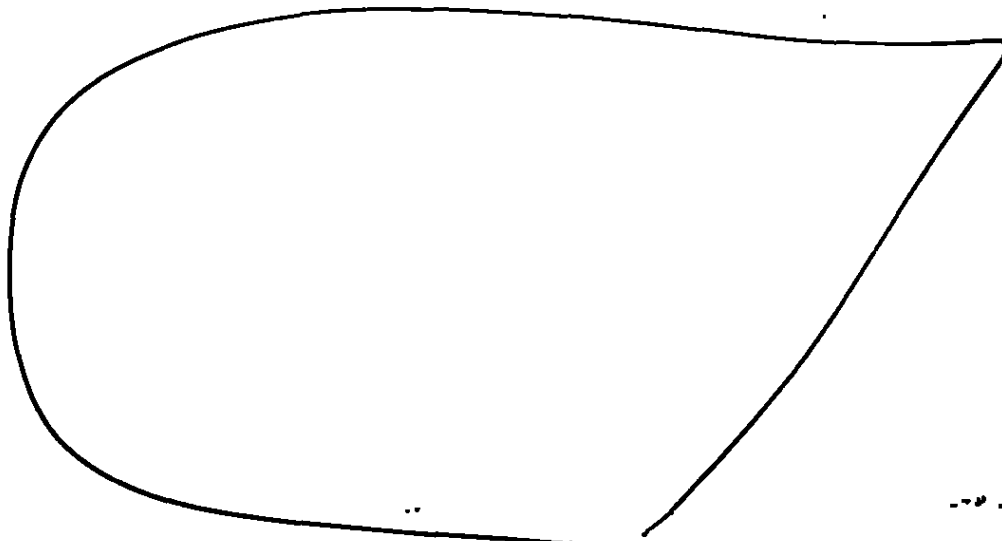
Por medio del presente escrito, y actuando en mi calidad de apoderado principal, me permito manifestarles que SUSTITUYO en favor del Dr. **LUIS FELIPE CASTILLO GIBSON** identificado con Cédula de Ciudadanía No. 79'397.879 de Bogotá y Tarjeta Profesional No. 68.995 del C.S.J. los poderes que me han sido conferidos por las sociedades **COATING SYSTEMS LABORATORIES, INC. y NORTHERN FILTER MEDIA, INC.** domiciliadas en 221 East Chilton Drive, Chandler, Arizona, E.U.A. y Pettibone Avenue, Muscatine, Iowa, E.U.A.

El Dr. Castillo Gibsone tendrá todas las facultades otorgadas en el poder conferido por la sociedad solicitante.

De Ustedes Atentamente,

GERMAN CASTILLO GRAU
C.C. No. 17'017.671 de Bogotá
T.P. No. 2.978 del C.S.J.

El anterior memorial fue presentado personalmente por
Germán de Jesús Castillo Grau
quien se identificó con C. de E. No. 17017571
de Bogotá
Tarjeta Profesional No. 2978-65 del 15
Bogotá, D. E., 19 JUL 2006



June 08, 2006

IOWA

SECRETARY OF STATE

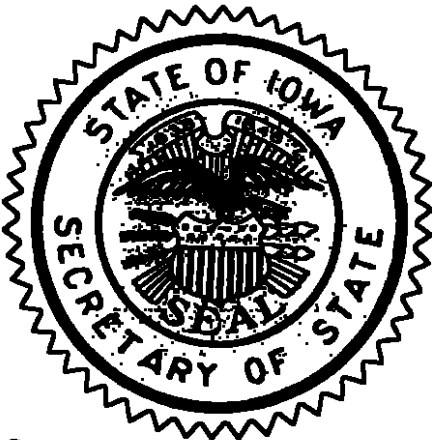
TOWNSEND TOWNSEND & CREW LLP
S. DOST
12730 HIGH BLUFF DR STE 400
SAN DIEGO, CA 92130 USA

APOSTILLE
(Convention de La Hague du 5 octobre 1961)

- 1 Country: United States of America
- 2 This public document has been signed by: P. MONHANA
- 3 Acting in the capacity of: NOTARY PUBLIC
- 4 Bearing the seal/stamp: NOTARY PUBLIC IN AND FOR THE STATE OF IOWA

CERTIFIED

- 5 at: DES MOINES, IOWA, UNITED STATES OF AMERICA
- 6 date: JUNE 8, 2006
- 7 by: the Secretary of State of the State of Iowa, United States of America
- 8 No. 06-043232
- 9 Seal
- 10 Signature



Chester J. Culver

CHESTER J. CULVER SECRETARY OF STATE





No. W00417488
Date: 06/05/2006

SECRETARY OF STATE

490 DP-000000594
NORTHERN FILTER MEDIA, INC.

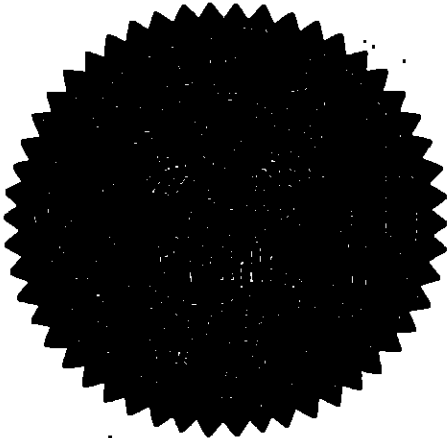
ACKNOWLEDGEMENT OF DOCUMENT FILED

The Secretary of State acknowledges receipt of the following document

Restated Articles of Incorporation

The document was filed on February 24, 2005, at 10:43 AM, to be effective as of February 24, 2005, at 10:43 AM.

The amount of \$50.00 was received in full payment of the filing fee.



A handwritten signature in black ink, reading "Chester J. Culver". The signature is fluid and cursive, with the first letters of the first and last names being capitalized and prominent.

CHESTER J. CULVER SECRETARY OF STATE



Printed on
Recycled Paper

625101 PART10 #001SELF1 2 22103

ARTICLES OF RESTATEMENT
OF THE ARTICLES OF INCORPORATION OF
NORTHERN GRAVEL COMPANY

594

TO THE SECRETARY OF STATE OF THE STATE OF IOWA:

Pursuant to the provisions of Section 490.1007 of the Iowa Business Corporation Act, the undersigned corporation (the "Corporation") has adopted the Restated Articles of Incorporation, consisting of three pages, which are attached and incorporated by reference, and the undersigned officer of the Corporation certifies as follows:

1. The present name of the Corporation is Northern Gravel Company. Its name under the Restated Articles of Incorporation attached is Northern Filter Media, Inc.
2. The restatement of the Articles of Incorporation does not provide for any exchange, reclassification, or cancellation of issued shares.
3. The Restated Articles of Incorporation consolidate all amendments of the Articles of Incorporation of the Corporation into a single document.
4. On January 15, 2005, the Restated Articles of Incorporation were duly approved by the shareholders of the Corporation in the manner required by the Iowa Business Corporation Act and by the Articles of Incorporation of the Corporation.

NORTHERN GRAVEL COMPANY

Dated: January 31, 2005

By David F. Reusswig
David F. Reusswig, President

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RESTATED ARTICLES OF INCORPORATION
OF
NORTHERN FILTER MEDIA, INC.

The following Restated Articles of Incorporation were adopted by the shareholders of the Corporation on the 15th day of January, 2005, in the manner prescribed by the Iowa Business Corporation Act:

ARTICLE 1

SECTION 1.01. NAME. The name of the Corporation is Northern Filter Media, Inc.

ARTICLE 2

SECTION 2.01. PURPOSES AND POWERS. The purposes for which the Corporation is organized include engaging in any or all lawful business. The Corporation shall have unlimited power to engage in and transact, and to do any lawful act concerning or incidental to, any or all such business.

ARTICLE 3

SECTION 3.01. AUTHORIZED SHARES. The aggregate number of shares which the Corporation shall have authority to issue is ten thousand (10,000) shares, consisting of one class of common stock, with no par value. The shares so authorized shall have unlimited voting rights. The holders of such shares shall be entitled to receive the net assets of the Corporation upon dissolution.

SECTION 3.02. RESTRICTIONS. The By-laws may contain any provisions restricting the transfer of any or all shares of the Corporation. A restriction does not affect shares issued before the restriction was adopted unless the holders of the shares are parties to the restriction agreement or voted in favor of the restriction.

ARTICLE 4

SECTION 4.01. NUMBER OF DIRECTORS. The number of Directors shall be fixed by the By-laws. The By-laws may fix the number of Directors either by stating the number, or a maximum and minimum number, or by providing that the number of Directors shall be the number determined by the shareholders from time to time as provided in the By-laws.

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SECTION 4.02. REMOVAL OF DIRECTORS. At any meeting of shareholders, the shareholders may remove any or all Directors at will, with or without cause and with or without notice, by the vote required by these Articles of Incorporation. The vacancy or vacancies in the Board of Directors caused by such removal may be filled as provided in the By-laws.

SECTION 4.03. DELEGATION; INDEMNIFICATION. Any or all duties and powers of the Board of Directors (including, without limitation, the duty and power to manage the business and affairs of the Corporation and all duties and powers imposed or conferred by the Iowa Business Corporation Act) may be delegated by the By-laws or by the Board of Directors to one or more officers, committees, or persons. The By-laws may contain provisions for indemnification and advancement of expenses.

SECTION 4.04. LIMITATION OF DIRECTOR'S LIABILITY. No Director shall be liable to the Corporation or its shareholders for money damages for any action taken, or any failure to take any action, as a Director, and the Corporation may indemnify a Director as provided in the Bylaws for any such liability to the Corporation or its shareholders or any liability to any person for such action or failure to take any action as a Director, except liability for any of the following:

- (a) The amount of a financial benefit received by a Director to which the Director is not entitled;
- (b) An intentional infliction of harm on the Corporation or the shareholders;
- (c) A violation of Section 490.833 of the Iowa Business Corporation Act; and
- (d) An intentional violation of criminal law.

Nothing in this Section 4.04 shall be construed to eliminate or limit the liability of a Director for an act or omission occurring prior to the date when this Section 4.04 became effective.

ARTICLE 5

SECTION 5.01. VOTE REQUIRED FOR ACTION. The affirmative vote of the holders of a majority of the total outstanding shares entitled to vote shall be required and shall be sufficient to adopt any motion or resolution or take any action at any meeting of shareholders (including, without limitation, election or removal of Directors; any amendment to these Articles of Incorporation; and any matter which is submitted to a vote at a meeting of shareholders, whether or not such submission is required by law, by action of the Board of Directors, or by agreement).

However, the By-laws may provide that action may be taken on any or all procedural matters by the vote of a lesser proportion of the shares.

This Section shall not be construed to require that any matter or action be submitted to a vote of shareholders or be authorized by the shareholders, if such submission or authorization would not

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be required in the absence of this Section.

SECTION 5.02. AMENDMENTS TO ARTICLES OF INCORPORATION. The shareholders reserve the right from time to time to amend these Articles of Incorporation, by the vote required by these Articles of Incorporation and in the manner now or hereafter permitted by the Iowa Business Corporation Act or other applicable law, whether or not the amendment constitutes or results in a fundamental change in the purposes or structure of the Corporation or in the rights or privileges of shareholders or others or in any or all of the foregoing. All rights and privileges of shareholders or others are subject to this reservation.

Any proposed amendment to these Articles of Incorporation may be modified or revised in any manner and to any extent by the shareholders at the meeting at which the proposed amendment to the Articles of Incorporation is submitted to the shareholders. If the proposed amendment as modified or revised is adopted by the shareholders, it shall be effective even though the modification or revision is proposed at the meeting and was not included in the notice or summary of the proposed amendment.

Wherever used in these Articles of Incorporation with respect to the Articles of Incorporation, the word "amend," "amended," or "amendment" includes and applies to the amendment, alteration, or repeal of any or all provisions of the Articles of Incorporation or the adoption of new or restated Articles of Incorporation.

SECTION 5.03. EFFECT OF ARTICLES OF INCORPORATION AND BY-LAWS. Each shareholder, by the act of becoming or remaining a shareholder of the Corporation or acquiring additional shares of the Corporation, shall be deemed to have accepted and agreed to all provisions of these Articles of Incorporation and the By-laws, as amended from time to time. These Articles of Incorporation and the By-laws shall constitute a contract among the shareholders and the Corporation, which may be amended as provided in these Articles of Incorporation and the By-laws.

Any shareholder, regardless of the period of time during which he or she has been a shareholder, shall have the right to examine the Articles of Incorporation and By-laws of the Corporation in person or by agent or attorney at any reasonable time and to make extracts. Upon written request of any shareholder, the Corporation shall mail a copy of the Articles of Incorporation and By-laws to him or her within a reasonable time.

NORTHERN FILTER MEDIA, INC.

first and second of January 2005

Dated: January 31, 2005

By David F. Reusswig
David F. Reusswig, President

0446902 Restated Articles of Incorporation

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APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

This public document

2. has been signed by H. L. Jackson

3. acting in the capacity of Certifying Officer

4. bears the seal/stamp of Patent and Trademark Office

Certified

5. at Washington, D.C.

6. the twenty-second of March, 2006

7. by *Assistant Authentication Officer, United States Department of State*

8. No. 06015093-1

9. Seal/Stamp:

10. Signature:

Sonya N. Johnson

60
X

A 1421900

THE UNITED STATES OF AMERICA

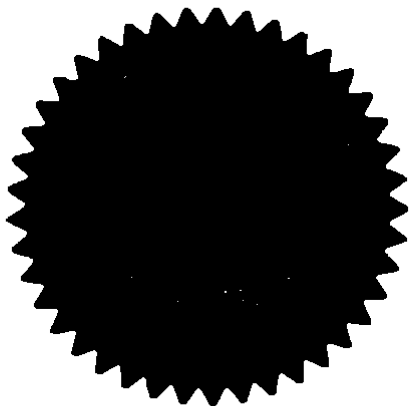
TO ALL TO WHOM THESE PRESENTS SHALL COME:

**UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office**

February 03, 2006

**THIS IS TO CERTIFY THAT ANNEXED IS A TRUE COPY FROM THE
RECORDS OF THIS OFFICE OF A DOCUMENT RECORDED ON
September 14, 2004**

**By Authority of the
Under Secretary of Commerce for Intellectual Property
and Director of the United States Patent and Trademark Office**




**H. L. JACKSON
Certifying Officer**

61
A

Attorney Docket No. 020511-000310US

Form PTO-1595 (Rev. 06/04)
OMB No. 0851-0027 (exp. 8/30/2008)U.S. DEPARTMENT OF COMMERCE
United States Patent and Trademark OfficeRECORDATION FORM COVER SHEET
PATENTS ONLY

To the Director of the U.S. Patent and Trademark Office: Please record the attached documents or the new address(es) below.

1. Name of conveying party(ies)/Execution Date(s):

William Peterson
Renee E. Berman

Execution Date(s) 08/02/04

Additional name(s) of conveying party(ies) attached? ☒ Yes ☐ No

3. Nature of conveyance:

- ☒ Assignment ☐ Merger
☐ Security Agreement ☐ Change of Name
☐ Government Interest Assignment
☐ Executive Order 9424, Confirmatory License
☐ Other

2. Name and address of receiving party(ies)

COATING SYSTEMS LABORATORIES,

Name: INC.

Internal Address:

Street Address: 211 E. Chilton Drive

City: Chandler

State: AZ

Country: United States Zip: 85076-0388

Additional name(s) & address(es) attached? ☐ Yes ☒ No

4. Application or patent number(s):

☐ This document is being filed together with a new application.

A. Patent Application No.(s)

10/850,121

B. Patent No.(s)

Additional numbers attached? ☐ Yes ☒ No

5. Name and address to whom correspondence concerning document should be mailed:

Name: Kenneth E. Jenkins, Ph.D.

Internal Address:

TOWNSEND AND TOWNSEND AND CREW LLP

Street Address: Two Embarcadero Center,
Eighth Floor

City: San Francisco

State: California Zip: 94111-3834

Phone Number: (415) 576-0200

Fax Number: (415) 576-0300

Email Address: @townsend.com

6. Total number of applications and patents involved:

1

7. Total fee (37 CFR 1.21(h) & 3.41) \$ 40.00

- ☐ Authorized to be charged by credit card
☒ Authorized to be charged to deposit account
☐ Enclosed
☐ None required (government interest not affecting title)

8. Payment Information

a. Credit Card Last 4 numbers
Expiration Date

b. Deposit Account Number 20-1430

Authorized User Name Townsend and
Townsend and Crew LLP

9. Signature:

Kenneth E. Jenkins, Ph.D.

Name of Person Signing · Atty. Reg. No. 51,846

09/13/04
DateTotal number of pages including cover
sheet, attachments, and documents:

4

Documents to be recorded (including cover sheet) should be filed to (703) 305-6000, or mailed to:
Mail Stop Assignment Recordation Services, Director of the USPTO, P.O. Box 1450, Alexandria, VA 22313-1450

CH \$40.00 201430 10350121

700114415

PATENT
REEL: 015138 FRAME: 0695

Attorney Docket No.: 020511-00031008

ASSIGNMENT OF PATENT APPLICATION**JOINT**

WHEREAS, William Peterson of 3126 E. Amber Ridge Way, Phoenix, AZ 85048; Renee E. Berman of 1600 N. Saba St., #110, Chandler, AZ 85225, hereinafter referred to as "Assignors," are the inventors of the invention described and set forth in the below-identified application for United States Letters Patent:

Title of Invention: **ANTIMICROBIAL QUATERNARY AMMONIUM
ORGANOSILANE COATINGS**

Date(s) of execution of Declaration:

Filing Date: **May 19, 2004**

Application No.: **10/850,121; and**

WHEREAS, COATING SYSTEMS LABORATORIES, INC., a corporation of the state of Arizona, located at 211 E. Chilton Drive, Chandler, AZ 85076-0386, hereinafter referred to as "ASSIGNEE," is desirous of acquiring an interest in the invention and application and in any U.S. Letters Patent and Registrations which may be granted on the same;

For good and valuable consideration, receipt of which is hereby acknowledged by Assignors, Assignors have assigned, and by these presents do assign to Assignee all right, title and interest in and to the invention and application and to all foreign counterparts (including patent, utility model and industrial designs), and in and to any Letters Patent and Registrations which may hereafter be granted on the same in the United States and all countries throughout the world, and to claim the priority from the application as provided by the Paris Convention. The right, title and interest is to be held and enjoyed by Assignee and Assignee's successors and assigns as fully and exclusively as it would have been held and enjoyed by Assignors had this Assignment not been made, for the full term of any Letters Patent and Registrations which may be granted thereon, or of any division, renewal, continuation in whole or in part, substitution, conversion, reissue, prolongation or extension thereof.

Assignors further agree that they will, without charge to Assignee, but at Assignee's expense, (a) cooperate with Assignee in the prosecution of U.S. Patent applications and foreign counterparts on the invention and any improvements, (b) execute, verify, acknowledge and deliver all such further papers, including patent applications and instruments of transfer, and (c) perform such other acts as Assignee lawfully may request to obtain or maintain Letters Patent and Registrations for the invention and improvements in any and all countries, and to vest title thereto in Assignee, or Assignee's successors and assigns.

Assignors hereby authorize and request Townsend and Townsend and Crew LLP, Two Embarcadero Center, Eighth Floor, San Francisco, CA 94111-3834, to insert herein above the application number and filing date of said application when known.

**PATENT
REEL: 015138 FRAME: 0696**

63
28

Assignment
Attorney Docket No.: 020511-000310US
Page 2

IN TESTIMONY WHEREOF, Assignors have signed their names on the dates indicated.

Dated: Sept 2 2004


William Peterson

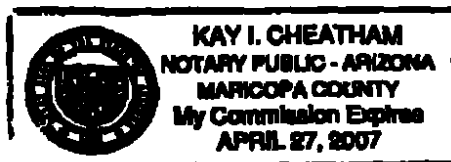
STATE OF ARIZONA)
COUNTY OF MARICOPA) ss.

On September 2, 2004, before me, KAY I. CHEATHAM,
personally appeared William Peterson, personally known to me (or proved to me on the basis of
satisfactory evidence) to be the person whose name is subscribed to the within instrument, and acknowledged to me
that he/she executed the same in his/her authorized capacity, and that by his/her signature on the instrument the
person, or the entity upon behalf of which the person acted, executed the instrument.

WITNESS my hand and official seal.


NOTARY PUBLIC

My Commission Expires: 4/27/07



PATENT
REEL: 015138 FRAME: 0697

Assignment
Attorney Docket No.: 020511-000310US
Page 3

IN TESTIMONY WHEREOF, Assignors have signed their names on the dates indicated.

Dated: 9/2/04

Renee E. Berman
Renee E. Berman

STATE OF ARIZONA
COUNTY OF MARICOPA

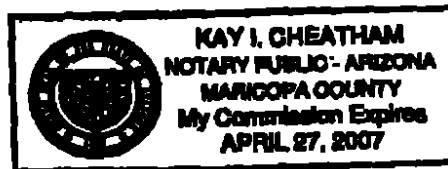
ss.

On SEPTEMBER 2, 2004, before me, KAY I. CHEATHAM, personally appeared Renee E. Berman, personally known to me (or proved to me on the basis of satisfactory evidence) to be the person whose name is subscribed to the within instrument, and acknowledged to me that he/she executed the same in his/her authorized capacity, and that by his/her signature on the instrument the person, or the entity upon behalf of which the person acted, executed the instrument.

WITNESS my hand and official seal.

Kay I. Cheatham
NOTARY PUBLIC

My Commission Expires: 4/27/07



60269382 v1

RECORDED: 09/14/2004

PATENT
REEL: 015138 FRAME: 0698

JK

APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

This public document

2. has been signed by H. L. Jackson

3. acting in the capacity of Certifying Officer

4. bears the seal/stamp of Patent and Trademark Office

Certified

5. at Washington, D.C.

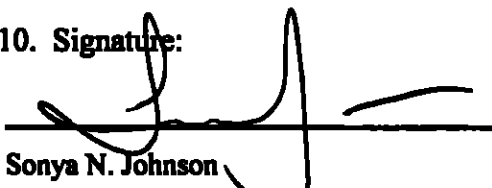
6. the twenty-second of March, 2006

7. by Assistant Authentication Officer, United States Department of State

8. No. 06015093-2

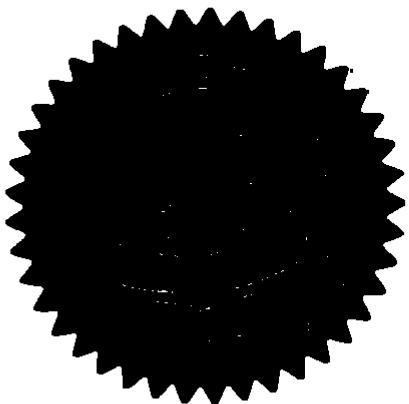
9. Seal/Stamp:

10. Signature:



Sonya N. Johnson

A 1431908

**THE UNITED STATES OF AMERICA****TO ALL TO WHOM THESE PRESENTS SHALL COME:****UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office****February 03, 2006****THIS IS TO CERTIFY THAT ANNEXED IS A TRUE COPY FROM THE
RECORDS OF THIS OFFICE OF A DOCUMENT RECORDED ON
January 12, 2005****By Authority of the
Under Secretary of Commerce for Intellectual Property
and Director of the United States Patent and Trademark Office****H. L. JACKSON
Certifying Officer**

Attorney Docket No. 020611-000310US

Form PTO-1593 (Rev. 06/04)
OMB No. 0661-0027 (exp. 8/30/2005)U.S. DEPARTMENT OF COMMERCE
United States Patent and Trademark OfficeRECORDATION FORM COVER SHEET
PATENTS ONLY

To the Director of the U.S. Patent and Trademark Office: Please record the attached document(s) or the new address(es) below.

1. Name of conveying party(ies)/Execution Date(s):

COATING SYSTEMS LABORATORIES,
INC.Execution Date(s) December 15, 2004Additional name(s) of conveying party(ies) attached? ☐ Yes ☒ No

3. Nature of conveyance:

- ☒ Assignment ☐ Merger
☐ Security Agreement ☐ Change of Name
☐ Government Interest Assignment
☐ Executive Order 8424, Confirmatory License
☐ Other _____

2. Name and address of receiving party(ies)

Name: NORTHERN GRAVEL COMPANY

Internal Address: _____

Street Address: 2508 Pettibone AvenueCity: MuscatineState: IACountry: U.S. Zip: 52761Additional name(s) & address(es) attached? ☐ Yes ☒ No

4. Application or patent number(s):

☐ This document is being filed together with a new application.

A. Patent Application No.(s)

10/850,121

B. Patent No.(s)

Additional numbers attached? ☐ Yes ☒ No

5. Name and address to whom correspondence concerning document should be mailed:

Name: Kenneth E. Jenkins, Ph.D.

Internal Address: _____

TOWNSEND AND TOWNSEND AND CREW LLPStreet Address: Two Embarcadero Center,
Eighth FloorCity: San FranciscoState: California Zip: 94111-3834Phone Number: (858) 360-8100Fax Number: (415) 576-0300Email Address: kjenkins@townsend.com

6. Total number of applications and patents involved:

17. Total fee (37 CFR 1.21(h) & 3.41) \$ 40.00

- ☐ Authorized to be charged by credit card
☒ Authorized to be charged to deposit account
☐ Enclosed
☐ None required (government interest not affecting title)

8. Payment Information

a. Credit Card Last 4 numbers _____
Expiration Date _____b. Deposit Account Number 20-1430Authorized User Name Townsend andTownsend and Crew LLP9. Signature: Kenneth E. Jenkins

Signature

Kenneth E. Jenkins, Ph.D.

Name of Person Signing Atty. Reg. No. 51,848

January 12, 2005

Date

Total number of pages including cover sheet, attachments, and documents: 4Documents to be recorded (including cover sheet) should be sent to (703) 305-5000, or mailed to:
Mail Stop Assignment Recordation Services, Director of the USPTO, P.O. Box 1468, Alexandria, VA 22313-1468

700145382

PATENT
REEL: 016589 FRAME: 0009

H

Attorney Docket No.: 020511-000310US

ASSIGNMENT

WHEREAS, COATING SYSTEMS LABORATORIES, INC., a corporation of the state of Arizona, located at 211 E. Chilton Drive, Chandler, AZ 85076-0386, hereinafter referred to as "ASSIGNOR," is the owner of all rights in certain new and useful improvements as described and set forth in the below-identified application for United States Letters Patent:

Title of Invention: ANTIMICROBIAL QUATERNARY AMMONIUM
ORGANOSILANE COATINGS

Filing Date: May 19, 2004

Serial No.: 10/850,121

WHEREAS, NORTHERN GRAVEL COMPANY, located at 2509 Pettibone Avenue, Muscatine, Iowa 52761, hereinafter referred to as "ASSIGNEE," wants to acquire a FIFTY PERCENT (50%) interest in the invention and application and in any Letters Patent and Registrations that may be granted on the same;

For good and valuable consideration, receipt of which is hereby acknowledged by Assignor, Assignor has assigned, and by these presents does assign to Assignee a FIFTY PERCENT (50%) interest in all right, title and interest in and to the invention and application and to all foreign counterparts (including patent, utility model and industrial designs), and in and to any Letters Patent and Registrations which may hereafter be granted on the same in the United States and all countries throughout the world, and to claim the priority from the application as provided by the Paris Convention. The FIFTY PERCENT (50%) right, title and interest is to be held and enjoyed by Assignee and Assignee's successors and assigns as fully and exclusively as it would have been held and enjoyed by Assignor had this assignment not been made, for the full term of any Letters Patent and Registrations which may be granted thereon, or of any division, renewal, continuation in whole or in part, substitution, conversion, reissue, prolongation or extension thereof.

Assignor further agrees that Assignor will, without charge to Assignee, but at Assignee's expense, (a) cooperate with Assignee in the prosecution of U.S. Patent applications and foreign counterparts on the invention and any improvements, (b) execute, verify, acknowledge and deliver all such further papers, including patent applications and instruments of transfer and (c) perform such other acts as Assignee lawfully may request to obtain or maintain Letters Patent and Registrations for the invention and improvements in any and all countries, and to vest title thereto in Assignee, or Assignee's successors and assigns.

Assignor hereby authorizes and requests Townsend and Townsend and Crew LLP, Two Embarcadero Center, Eighth Floor, San Francisco, CA 94111-3834, to insert herein above the application number and filing date of said application when known.

IN TESTIMONY WHEREOF, this Assignment is executed this 15th day of December, 2005.

BY: [Signature]Title: CEO & President

PATENT
REEL: 015589 FRAME: 0010

Assignment

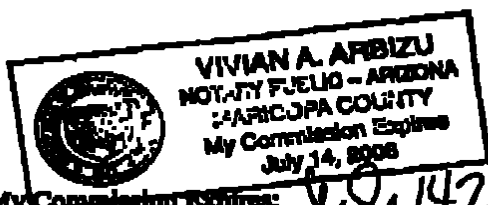
Attorney Docket No.: 020511-000310US

Page 2

STATE OF Arizona)
COUNTY OF Maricopa)

On 15 Dec 2004 before me, VIVIAN A. ARBIZU, personally appeared William P. Peltier, personally known to me (or proved to me on the basis of satisfactory evidence) to be the person whose name is subscribed to the within instrument, and acknowledged to me that he/she executed the same in his/her authorized capacity, and that by his/her signature on the instrument the person, or the entity upon behalf of which the person acted, executed the instrument.

WITNESS my hand and official seal.



Vivian A. Arbizu
NOTARY PUBLIC

My Commission Expires: 8/14/2008

60307352 v1

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DA 1472350



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

June 01, 2006

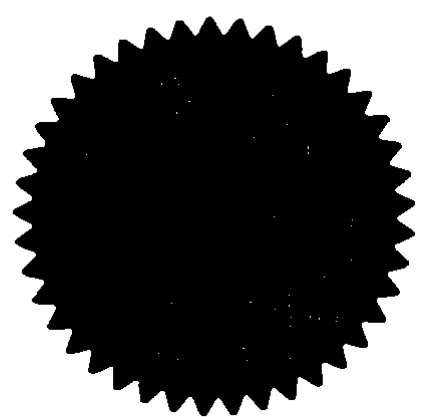
THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 10/850,121

FILING DATE: May 19, 2004

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS US10/850,121

**By Authority of the
Under Secretary of Commerce for Intellectual Property
and Director of the United States Patent and Trademark Office**



T. Wallace
T. WALLACE
Certifying Officer

71

UTILITY
PATENT APPLICATION
TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	020511-000310US
First Inventor	Peterson, William
Title	ANTIMICROBIAL QUATERNARY AMMONIUM ORGANOSILANE COATINGS
Express Mail Label No.	EV 332111981 US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. ☒ Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)
2. ☒ Applicant claims small entity status.
See 37 CFR 1.27.
3. ☒ Specification (Total Pages 34)
(preferred arrangement set forth below)
 - Descriptive title of the invention
 - Cross Reference to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to sequence listing, a table, or a computer program listing appendix
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
4. ☒ Drawing(s) (35 U.S.C. 113) (Total Sheets 6)
5. Oath or Declaration (Total Pages 1)
 - a. ☐ Newly executed (original or copy)
 - b. ☐ Copy from a prior application (37 CFR 1.63 (d))
(for a continuation/divisional with Box 18 completed)
 - c. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s)
named in the prior application, see 37 CFR
1.63(d)(2) and 1.33(b).
6. ☒ Application Data Sheet. See 37 CFR 1.78

ADDRESS TO

Mail Stop Patent Application
Commissioner for Patents
P.O. Box 1480
Alexandria, VA 22313-1480

7. ☐ CD-ROM or CD-R in duplicate, large table or
Computer Program (Appendix)
8. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
 - a. ☐ Computer Readable Form (CRF)
 - b. Specification Sequence Listing on:
 - i. ☐ CD-ROM or CD-R (2 copies); or
 - ii. ☐ Paper number of pages
 - c. ☐ Statements verifying identity of above copies

ACCOMPANYING APPLICATIONS PARTS

9. ☐ Assignment Papers (cover sheet & document(s))
10. ☐ 37 CFR 3.73(b) Statement ☐ Power of
(when there is an assignee) Attorney
11. ☐ English Translation Document (if applicable)
12. ☐ Information Disclosure ☐ Copies of IDS
Statement (IDS)/PTO-1449 Citations
13. ☐ Preliminary Amendment
14. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
15. ☐ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
16. ☐ Nonpublication Request under 35 U.S.C. 122
(b)(2)(B)(i). Applicant must attach form PTO/SB/35
or its equivalent
17. ☐ Other.

18. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in the first sentence of the specification following the title, or in an Application Data Sheet under 37 CFR 1.78:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP)

of prior application No: _____

Prior application information:

Examiner _____

Art Unit: _____

For CONTINUATION OF DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

19. CORRESPONDENCE ADDRESS

☒ Customer Number

20350

OR ☐ Correspondence address below

Name

Address

City

State

Zip Code

Country

Telephone

Fax

Name (Print/Type)

M. Henry Helms

Registration No. (Attorney/Agent)

28,219

Signature

Date

May 19, 2004

60219845 v1

72

FEE TRANSMITTAL for FY 2004

Effective 10/01/2003. Patent fees are subject to annual revision.

☒ Applicant claims small entity status. See 37 CFR 1.27TOTAL AMOUNT OF PAYMENT (\$)
457

Complete if Known

Application Number	
Filing Date	May 18, 2004
First Named Inventor	Peterson, William
Examiner Name	
Art Unit	
Attorney Docket No.	020611-000310US

METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit Card ☐ Money Order ☐ Other ☐ None☒ Deposit Account:Deposit
Account
Number

20-1430

Deposit
Account
Name

Townsend and Townsend and Crew LLP

The Director is authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☒ Credit any overpayments☒ Charge any additional fee(s) or any underpayment of fee(s)☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.

FEE CALCULATION

1. BASIC FILING FEE

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1001	770	2001	385	Utility filing fee	385
1002	340	2002	170	Design filing fee	
1003	630	2003	265	Plant filing fee	
1004	770	2004	385	Release filing fee	
1005	160	2005	80	Provisional filing fee	

SUBTOTAL (1)

3385

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

Total Claims	Extra Claims	Fee from below	Fee Paid
28	-30** = 0	0	072
Independent Claims	1	-3** = 0	043
Multiple Dependent			

Large Entity		Small Entity		Fee Description
Fee Code	Fee (\$)	Fee Code	Fee (\$)	
1202	18	2202	9	Claims in excess of 20
1201	86	2201	43	Independent claims in excess of 3
1203	280	2203	145	Multiple dependent claims, if not paid
1204	55	2204	43	** Release independent claims over original patent
1205	18	2205	9	** Release claims in excess of 20 and over original patent

SUBTOTAL (2)

372

**or number previously paid, if greater; For Reissues, use above

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1061	130	2051	65	Surcharge - late filing fee or oath	
1062	80	2052	25	Surcharge - late provisional filing fee or cover sheet	
1063	130	1063	130	Non-English specification	
1812	2,520	1812	2,520	For filing a request for reexamination	
1804	820*	1804	820*	Requesting publication of SPR prior to Examiner action	
1806	1,840*	1806	1,840*	Requesting publication of SPR after Examiner action	
1261	110	2261	55	Extension for reply within first month	
1252	420	2252	210	Extension for reply within second month	
1253	980	2253	475	Extension for reply within third month	
1254	1,480	2254	740	Extension for reply within fourth month	
1265	2,010	2255	1,005	Extension for reply within fifth month	
1401	330	2401	165	Notice of Appeal	
1402	330	2402	165	Filing a brief in support of an appeal	
1403	280	2403	145	Request for oral hearing	
1461	1,510	1461	1,510	Petition to institute a public use proceeding	
1462	110	2452	55	Petition to revise - unavoidable	
1463	1,330	2463	665	Petition to revise - unintentional	
1801	1,330	2501	665	Utility issue fee (or release)	
1802	480	2502	240	Design issue fee	
1803	640	2503	320	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	80	1807	80	Petitions related to provisional applications	
1806	180	1806	180	Submission of Information Disclosure Sheet	
8021	40	8021	40	Recording each patent assignment per property (less number of properties)	
1809	770	2809	385	Filing a submission after final rejection (37 CFR § 1.129(a))	
1810	770	2810	385	For each additional invention to be examined (37 CFR § 1.129(b))	
1801	770	2801	385	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited examination of a design application	

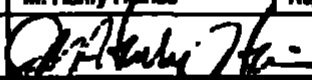
Other fee (specify)

*Reduced by Basic Filing Fee Paid SUBTOTAL (3)

(\$)

SUBMITTED BY

Complete if applicable

Name (Print/Type)	M. Henry Haines	Registration No. (Attorney/Agent)	28,219	Telephone	415-575-0200
Signature				Date	May 18, 2004

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60219885 v1

Attorney Docket No.: 020511-000310US

PATENT APPLICATION

**ANTIMICROBIAL QUATERNARY AMMONIUM ORGANOSILANE
COATINGS**

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**ANTIMICROBIAL QUATERNARY AMMONIUM ORGANOSILANE
COATINGS**

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application is related to United States Provisional Patent Application No. 60/472,429, filed May 22, 2003, and claims all benefits legally available therefrom. Provisional Patent Application No. 60/472,429 is hereby incorporated in its entirety for all purposes capable of being served thereby.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] This invention relates to methods and compositions for reducing the number of microorganisms in a liquid using a solid phase carrier coated with a quaternary ammonium organosilane coating.

Description of the Prior Art

[0003] Quaternary ammonium organosilanes have been employed in a wide variety of applications. They have been used effectively in eliminating and reducing microorganismal contamination when applied to a variety of surfaces including metal, glass, plastics, rubber, ceramics and fabrics including cellulose, cotton, acetates and nylon.

[0004] Commercial quaternary ammonium organosilanes are available as 42% active material in methanol under the trademark Dow Corning 5700 (3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride) by Aegis Environmental Management, Inc. of Midland, MI and Requat 1977 (3-(trimethoxysilyl)-propyldidecylmethyl ammonium chloride) by Sanitized Inc. of New Preston, CT. Octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride (Cat. No. SIO6620.0) as a 60% active solution in methanol, tetradecyldimethyl(3-tri-methoxysilylpropyl) ammonium chloride (Cat. No. SIT7090.0) as a 50% solution in methanol and didecylmethyl(3-trimethoxysilylpropyl) ammonium chloride (Cat. No. SID3392.0) as a 42% solution in methanol are offered by Gelest, Inc. of Tullytown, PA. They are often applied from solvent solutions such as lower alcohols.

[0005] Organosilicon ammonium compounds were first taught by Roth in U.S. Pat. No. 3,560,385. The use of these compounds for antimicrobial purposes is taught in U.S.

Pat. 3,730,701 to Isquith et al. They teach that neutral to alkaline pH values were more effective in algae control, but no claims for stability of aqueous solutions were made.

[0006] Algae inhibition was also taught in U.S. Pat. Nos. 3,794,736 and 3,860,709. The inhibition of algae growth on solid surfaces such as cellulose acetate following treatment with organosilane quaternary ammonium materials was described by Abbott et al. in U.S. Pat. No. 3,817,739. Abbott et al. in U.S. Pat. No. 3,865,728 again describes algicidal reduction on fibrous materials including polyesters as well as cellulose acetate. G. Kinstedt in U.S. Pat. No. 4,005,025 claims organosilane quaternaries as being useful in imparting soil release properties to hard surfaces in detergent applications such as dishwashing liquids and general hard surface cleaners, but makes no claims for antimicrobial activity.

[0007] U.S. Pat. 4,005,028 to Heckert et al. similarly teaches detergent compositions containing zwitterionic or ampholytic detergents and quaternized organosilanes. Similarly, U.S. Pat. No. 4,005,030 by D. Heckert and D. Watt teach detergent formulations useful as oven cleaners, window cleaners or toilet bowl cleaners. No antimicrobial claims are present in the '025, '028 and '030 Patents.

[0008] In U.S. Pat. No. 4,282,366 organosilicon ammonium compounds are used to render paper substrates resistant to growth of microorganisms. Similarly, Klein in U.S. Pat. No. 4,394,378 claims 3-(trimethoxysilyl)propyldidecylmethyl ammonium chloride as effective against bacteria and fungi on siliceous surfaces, wood, metal, leather, rubber, plastic and textiles.

[0009] Other applications for these compounds include paint additives and shoe treatments in U.S. Pat. No. 4,393,378, dentifrice additives in U.S. Pat. No. 4,161,518, and in contact lens disinfectant solution in U.S. Pat. No. 4,615,882. Canadian Patent No. 1,217,004 to Hardy teaches these compounds are antimicrobial when added to bleach such as sodium hypochlorite and can be used as hard surface cleaners.

[0010] U.S. Pat. No. 4,406,892 describes treatment of cellulosic fabrics to prevent the growth of disease causing organisms. Similarly, Burtil et al. in U.S. Pat. 4,421,796 teach a method of treating textile fibers with a mixture of quaternized organosilane compositions in an emulsion containing polydimethylsiloxanes to improve removal of oily soil.

[0011] In U.S. Pat. No. 4,467,013 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride is taught as being useful in the treatment of surgical gowns, dressings and bandages.

Homan in U.S. Pat. 4,564,456 utilizes organosilicon quaternary ammonium compounds to treat water and inhibit corrosion and metal deposition. Hair conditioning compositions containing 3-(trimethoxysilyl)propyl-dimethyloctadecyl ammonium chloride, when applied at pH 8-10 causing the hair to swell is taught by Stadnick in U.S. Pat. 4,567,039.

[0012] Aqueous emulsions formed by the use of certain organofunctional cationic silanes, including quaternary ammonium organosilanes such as 3-(trimethoxysilyl)propyl-dimethyloctadecyl ammonium chloride, are taught by Blehm et al. in U.S. Pat. No. 4,361,273. The disclosed oil-in-water emulsions allow the transfer of water immiscible liquids and silanes to the surface of certain substrates with the avoidance of any subsequent rewetting or resolubilization of the silane or water immiscible liquid and its subsequent loss from the surface. The water immiscible liquid utilized to prevent resolubilizing of the cationic silane away from the substrate may be silicone oils, waxes, hydrocarbons, glycols or aliphatic alcohols. The preparation of these emulsions utilize co-surfactants such as nonionic and cationic surfactants and require a homogenizer using high shear conditions and teach that the quaternized organosilane does not hydrolyze to the silanol while in its emulsion form and thus does not polymerize to an insoluble siloxane. These emulsions require a water immiscible liquid as described above with which the quaternized organosilane associates, and that a sufficient shear force, requiring specialized mixers, is necessary to form the emulsion they teach. Blehm et al. teaches the prepared emulsion is utilized to transfer the unhydrolyzed quaternized organosilane to the surface where it is protected against resolubilization by the water immiscible component.

[0013] The use of similar oil-in-water emulsion compositions in treating acne vulgaris and ringworm is taught in U.S. Pat. 4,908,355 to Gettings & White. This patent teaches a method of treating skin disorders through topical application to the epidermis of an oil-in-water emulsion in which there is a quaternary ammonium organosilane, specifically 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride and a low viscosity, low molecular weight water immiscible liquid silicone fluid, which causes the quaternized silane to penetrate the follicular orifices. The volatile silicone fluid is for the purpose of driving the silane into sebaceous glands and destroying the staphylococcal group of bacteria that may reside there. The formation of these emulsions are essentially the formulations taught in the foregoing '273 patent. This patent teaches the quaternized silane can be used neat, in an organic solvent or in aqueous solvent solutions. It further teaches a water immiscible component such as an oil, wax or grease must be present and included in the compositions

77
2A

applied to the skin. It does not teach homogeneous aqueous solutions of the quaternary ammonium organosilane nor demonstrate substantiveness and efficacy on skin. The ability of the silane to be applied directly to the skin from aqueous solutions and the ability for the silane to remain on the skin and continue to be antimicrobially active even after repeated rinsings or washings is not taught.

[0014] Glass beads treated with organosilane quaternary compounds are described in U.S. Pat. No. 4,682,992 as being used in air filters where antimicrobial qualities are desired. U.S. Pat. No. 4,781,974 teaches wet towelettes having as organosilicon quaternary ammonium compound substantive to the fibers, but does not teach it being transferred to surfaces or skin. Bryant in U.S. Pat. 4,797,420 teaches a formulation containing an alkyl dimethyl benzyl ammonium chloride, a nonionic surfactant and a lower alcohol such as isopropanol in water which is used as a disinfectant formulation.

[0015] U.S. Pat. 4,847,088 to Blank teaches a quaternary organosilane composition such as 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride when combined with an acid in water will increase the antimicrobial effect. Similar antimicrobial properties are claimed in U.S. Pat. No. 5,013,459 for a method and device to dispense ophthalmic fluids, the porous medium of which has been previously treated with an organosilicon quaternary ammonium material.

[0016] U.S. Pat. 5,411,585 to Avery et al. teaches further methods for the production of stable hydrolyzable organosilane quaternary ammonium compounds to render surfaces antimicrobial when applied as ingredients in hard surface cleaners.

[0017] Stabilized aqueous organosilane solutions, including quaternary ammonium organosilane compounds, with stability of weeks to months, are taught by Elferry et al. in U.S. Pat. 5,954,869. These compositions contain a polyol molecule having at least two hydroxy groups which are separated by no more than three intervening atoms and the organosilane. These compositions may be used to coat a food article, a fluid container or a latex medical article. Sugars are the most common stabilizer taught in this patent.

[0018] Antimicrobial skin preparations containing quaternary ammonium organosilanes are taught by Peterson et al. in U.S. Patent 6,613,755, which is herein incorporated by reference in its entirety for all purposes.

[0019] The prior art and open literature disclose the antimicrobial properties of quaternary ammonium organosilanes against a wide range of pathogens including, but not limited to: Gram Positive Bacteria such as *Citrobacter freundii*, *Citrobacter diversus*, *Corynebacterium diphtheriae*, *Diplococcus pneumoniae*, *Micrococcus sp. (I)*, *Micrococcus sp. (II)*, *Micrococcus sp. (III)*, *Mycobacterium spp.*, *Staphylococcus albus*, *Staphylococcus aureus*, *Staphylococcus citreus*, *Staphylococcus epidermidis*, *Streptococcus faecalis*, and *Streptococcus pyogenes*; Gram Negative Bacteria such as *Acinetobacter calcoaceticus*, *Enterobacter aerogenes*, *Enterobacter agglomerans (I)*, *Enterobacter agglomerans (II)*, *Escherichia coli*, *Klebsiella pneumoniae*, *Nisseria gonorrhoeae*, *Proteus mirabilis*, *Proteus morganii*, *Proteus vulgaris*, *Providencia spp.*, *Pseudomonas*, *Pseudomonas aeruginosa*, *Pseudomonas fragi*, *Salmonella choleraesuis*, *Salmonella enteritidis*, *Salmonella gallinarum*, *Salmonella paratyphi A*, *Salmonella schottmuelleri*, *Salmonella typhimurium*, *Salmonella typhosa*, *Serratia marcescens*, *Shigella flexnerie Type II*, *Shigella sonnei*, *Vibrio cholerae*; viruses such as Adenovirus Type IV, Feline Pneumonitis, Herpes Simplex Type I & II, HIV-1 (AIDS), Influenza A (Japan), Influenza A2 (Aichi), Influenza A2 (Hong Kong), Parainfluenza (Sendai), Poliovirus, Reovirus, Respiratory Syncytia; Fungi and Mold such as, *Alternaria alternate*, *Aspergillus niger*, *Aureobasidium pullulans*, *Candida albicans*, *Cladosporium cladosporioides*, *Drechslera australiensis*, *Gliomastix cerealis*, *Microsporum audouinii*, *Monilia grisea*, *Phoma fimeii*, *Plthomyces chartarum*, *Scolecobasidium humicola*, *Trychophyton interdigitale*, and *Trychophyton mentagrophytes*.

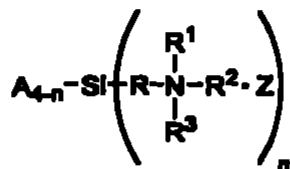
[0020] The open literature and the prior art cited above do not teach the use of a solid phase carrier coated with a quaternary ammonium organosilane coating to reduce the viable number of microorganisms in a liquid.

BRIEF SUMMARY OF THE INVENTION

[0021] The present invention provides methods and compositions for use in a variety applications, such as water purification and reduction of harmful microorganisms in liquid foodstuffs.

[0022] In one aspect, the present invention provides a method of reducing or eliminating the viable number of microorganisms in a liquid. The method includes contacting the liquid with a solid phase carrier coated with a quaternary ammonium organosilane coating.

[0023] In an exemplary embodiment, the quaternary ammonium organosilane reagent has the formula:



(I).

[0024] In Formula (I), A is selected from -OR⁴, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl. Where more than one A is present, each A is independently selected from the groups recited above or below.

[0025] R⁴ is selected from hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl.

[0026] R is selected from substituted or unsubstituted alkylene, substituted or unsubstituted heteroalkylene, substituted or unsubstituted cycloalkylene, substituted or unsubstituted heterocycloalkylene, substituted or unsubstituted arylene, and substituted or unsubstituted heteroarylene.

[0027] R¹, R², and R³ are independently selected from hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl.

[0028] Z is selected from fluoride, chloride, bromide, iodide, tosylate, hydroxide, sulfate and phosphate.

[0029] The symbol n is 1, 2 or 3.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] FIG. 1 illustrates the reduction in the viable number of bacteriophages by quaternary ammonium organosilane coated zeolite.

[0031] FIG. 2 illustrates the reduction in the viable number of (A) *K. terrigena* bacteria and (B) *E. Coli* bacteria by quaternary ammonium organosilane coated zeolite.

[0032] FIG. 3 illustrates the average reduction in the viable number of bacteria and bacteriophages by quaternary ammonium organosilane coated zeolite.

[0033] FIG. 4 illustrates the reduction in the viable number of algae by quaternary ammonium organosilane coated zeolite.

[0034] FIG. 5 illustrates the reduction in the viable number of protozoa parasites by quaternary ammonium organosilane coated zeolite.

[0035] FIG. 6 illustrates an experimental apparatus containing a column packed with quaternary ammonium organosilane coated zeolite for use in decreasing the viable number of microorganisms in a liquid.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0036] As used herein, the term "reducing the viable number of microorganisms," means reducing the number of microorganisms capable of growing, working, functioning, and/or developing adequately. The term includes, for example, reducing the overall number of microorganisms, reducing the number of active microorganisms (i.e. inactivating microorganisms), reducing the number of microorganisms able to reproduce, reducing the number of intact microorganisms, reducing the number of infectious agents, removal of microorganisms, inactivation of microorganisms; and/or and the like. "Eliminating the viable number of microorganisms" means reducing the viable number of microorganisms to zero.

[0037] The term "microorganism," as used herein, means an organism that, individually, can only be seen through a microscope. The term microorganism includes, for example, bacteria, fungi, actinomycetes, algae, protozoa, yeast, germs, ground pearls, nematodes, viruses, prions, and algae.

[0038] The abbreviations used herein have their conventional meaning within the chemical and biological arts.

[0039] Where chemical groups are specified by their conventional chemical formulae, written from left to right, they equally encompass the chemically identical substituents that would result from writing the structure from right to left, e.g., $-\text{CH}_2\text{O}-$ is equivalent to $-\text{OCH}_2-$.

[0040] The term "alkyl," by itself or as part of another substituent, means, unless otherwise stated, a straight (i.e. unbranched) or branched carbon chain containing at least one carbon, which may be fully saturated, mono- or polyunsaturated. An unsaturated alkyl group is one having one or more double bonds or triple bonds. An "unsubstituted alkyl" refers to branched

or unbranched alkyl groups wherein the backbone carbons are attached to hydrogen and/or other backbone carbon. The term "alkylene" refers to a divalent radical derivative of an alkyl.

[0041] A "backbone carbon" or "backbone heteroatom," as used herein, refers to a carbon or heteroatom, respectively, that is not at the point of attachment of an alkyl or heteroalkyl group, and which forms part of a branched or unbranched chain containing at least one carbon.

[0042] The term "alkoxy," refers to those alkyl groups attached to the remainder of the molecule via an oxygen atom.

[0043] The term "alkylether" refers to an alkyl having at least one carbon-oxygen-carbon linkage.

[0044] The term "hydroxy-substituted alkyl" refers to an alkyl having at least one attached hydroxyl group.

[0045] The term "amine-substituted alkyl" refers to an alkyl having at least one attached primary, secondary, or tertiary amine group.

[0046] The term "heteroalkyl," by itself or in combination with another term, means an alkyl having at least one heteroatom within the carbon chain. The heteroatom is selected from the group consisting of O, N, and S, wherein the nitrogen and sulfur atoms may optionally be oxidized and the nitrogen heteroatom may optionally be quaternized. The heteroatom(s) O, N, and S may be placed at any interior position of the heteroalkyl group or at the position at which the alkyl group is attached to the remainder of the molecule. Up to two heteroatoms may be consecutive, such as, for example, $-\text{CH}_2\text{-NH-OCH}_3$. Similarly, the term "heteroalkylene" by itself or as part of another substituent means a divalent radical derived from heteroalkyl. For heteroalkylene groups, heteroatoms can also occupy either or both of the chain termini.

[0047] An "unsubstituted heteroalkyl" refers to branched or unbranched heteroalkyl groups wherein the backbone carbons are attached to hydrogen, other backbone carbons, and/or backbone heteroatoms. The backbone heteroatoms are attached to hydrogen, backbone carbons, other backbone heteroatoms, and/ or oxygen (in the case of oxidized sulfur).

[0048] The terms "cycloalkyl" and "heterocycloalkyl", by themselves or in combination with other terms, represent, unless otherwise stated, cyclic versions of "alkyl" and "heteroalkyl", respectively. Additionally, for heterocycloalkyl, a heteroatom can occupy the position at which the heterocycle is attached to the remainder of the molecule. The terms "cycloalkylene" and "heterocycloalkylene" refer to the divalent derivatives of cycloalkyl and heterocycloalkyl groups, respectively.

[0049] The terms "halo" or "halogen," by themselves or as part of another substituent, mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom. Additionally, terms such as "haloalkyl," are meant to include monohaloalkyl and polyhaloalkyl.

[0050] The term "aryl" means, unless otherwise stated, a polyunsaturated, aromatic, hydrocarbon which can be a single ring or multiple rings (preferably from 1 to 3 rings) which are fused together or linked covalently. The term "heteroaryl" refers to aryl groups (or rings) that contain from one to four heteroatoms selected from N, O, and S, wherein the heteroatom occupies a ring vertex (also referred to herein as a "ring heteroatom"). The nitrogen and sulfur atoms are optionally oxidized, and the nitrogen atom(s) are optionally quaternized. A heteroaryl group can be attached to the remainder of the molecule through a carbon or heteroatom. The terms "arylene" and "heteroarylene" refer to the divalent derivatives of aryl and heteroaryl groups, respectively.

[0051] An "unsubstituted aryl" or "unsubstituted heteroaryl" refers to aryl and heteroaryl rings, respectively, in which the carbon atoms occupying ring vertices that are not at a point of attachment to the remainder of the molecule are attached only to hydrogen or other atoms occupying ring vertices. Heteroatoms occupying ring vertices that are not at a point of attachment to the remainder of the molecule are attached only to hydrogen, other atoms occupying ring vertices, or oxygen (in the case of oxidized ring heteroatoms).

[0052] The term "oxo" as used herein means an oxygen that is double bonded to a carbon atom.

[0053] A "liquid," as used herein, is a substance that flows freely, lacks crystal structure, and, unlike a gas, retains the same volume independent of the shape of its container at ambient temperature and pressure. An "aqueous liquid" refers to a liquid having a portion of water. Aqueous liquids suitable for the practice of the present invention include, for example, waste water and sewage water, fruit juices, milk, and medical fluids. Other suitable

fluids will be readily determined by those skilled in the art and are contemplated by the instant invention.

[0054] A "solid," as used herein, is a substance that does not dissolve in water at ambient temperature. Thus, a "solid phase carrier" is a carrier that is insoluble in water at ambient temperature.

Methods

[0055] In one aspect, the present invention provides a method of reducing or eliminating the viable number of microorganisms in a liquid. The method includes contacting the liquid with a solid phase carrier coated with a quaternary ammonium organosilane coating. The quaternary ammonium organosilane coating may reduce the viable number of microorganisms in a liquid by directly contacting the microorganisms.

[0056] A wide variety of solid phase carriers are useful in conjunction with the methods and compositions of the present invention. The solid phase carrier may be any appropriate dimension or shape, including, for example, a planar surface, the lining of tubing or pipe, or a roughly spherical particle. The solid phase carrier may also be any appropriate size, including, for example, a microscopic carrier, a carrier detectable with the naked eye, a roughly planar carrier with dimensions that are centimeters to meters in length, and roughly spherical carrier with a radius that is centimeters to meters in length.

[0057] The solid phase carrier is typically composed of one or more substance or material that is insoluble in liquid media (e.g. organic media, aqueous media, water, etc.). Exemplary materials include glass, silica, sand (e.g. manganese greensand and filter sand), quartz, flint, zeolite, anthracite, activated carbon, garnet, ilmenite, beryl, aluminum (including non-hydrous aluminum silicate (e.g. filter AG)), oxides of iron and titanium (e.g. ilmenite), diatomaceous earth, pozzolan (silicon/alumina material that occurs naturally and is produced as a byproduct of coal combustion), metal (e.g. tin), ceramic, and/or organic polymers and plastics (e.g. high density polyethylene (HDPE), polypropylene (PP) or polyvinyl chloride (PVC)).

[0058] In an exemplary embodiment, the liquid is contacted with an additional solid phase carrier. The additional solid phase carrier may be coated with a different quaternary ammonium organosilane coating than the solid phase carrier. The additional solid phase carrier may also be composed of a different material than the solid phase carrier.

Quaternary Ammonium Organosilane Reagents

[0059] The solid phase carriers of the current invention are coated with a quaternary ammonium organosilane coating. The quaternary ammonium organosilane coating is produced from a quaternary ammonium organosilane reagent. The quaternary ammonium organosilane reagent has the formula:



[0060] In Formula (I), A is selected from -OR⁴, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl. Where more than one A is present, each A is independently selected from the groups recited above or below.

[0061] R⁴ is selected from hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl.

[0062] R is selected from substituted or unsubstituted alkylene, substituted or unsubstituted heteroalkylene, substituted or unsubstituted cycloalkylene, substituted or unsubstituted heterocycloalkylene, substituted or unsubstituted arylene, and substituted or unsubstituted heteroarylene.

[0063] R¹, R², and R³ are independently selected from hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl.

[0064] Z is selected from fluoride, chloride, bromide, iodide, tosylate, hydroxide, sulfate and phosphate.

[0065] The symbol n is 1, 2 or 3.

[0066] In an exemplary embodiment, each substituted alkyl, substituted heteroalkyl, substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl, and substituted

heteroaryl described herein as possible A, R¹, R², R³, and R⁴ moieties are substituted only with at least one substituent independently selected from -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted 2 to 5 membered heteroalkyl, unsubstituted (C₅-C₇) membered cycloalkyl, unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl. For example, where A is a substituted (C₁-C₁₀)alkyl, the substituted (C₁-C₁₀)alkyl is substituted only with at least one substituent independently selected from -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted 2 to 5 membered heteroalkyl, unsubstituted (C₅-C₇) membered cycloalkyl, unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl.

[0067] In a related embodiment, each substituted alkyl, substituted heteroalkyl, substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl, and substituted heteroaryl described herein as possible A, R¹, R², R³, and R⁴ moieties are substituted only with at least one substituent independently selected from -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted 2 to 5 membered heteroalkyl, unsubstituted (C₅-C₇) membered cycloalkyl, unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl. In another related embodiment, each substituted alkyl, substituted heteroalkyl, substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl, and substituted heteroaryl described herein as possible A, R¹, R², R³, and R⁴ moieties are substituted only with at least one substituent independently selected from -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted (C₅-C₇) membered cycloalkyl, and unsubstituted phenyl. In yet another related embodiment, each substituted alkyl, substituted heteroalkyl, substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl, and substituted heteroaryl described herein as possible A, R¹, R², R³, and R⁴ moieties are substituted only with at least one unsubstituted (C₁-C₃)alkyl.

[0068] In another exemplary embodiment, each substituted alkylene, substituted heteroalkylene, substituted cycloalkylene, substituted heterocycloalkylene, substituted arylene, and substituted heteroarylene described herein as possible R moieties are substituted only with at least one substituent independently selected from -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted 2 to 5 membered heteroalkyl, unsubstituted (C₅-C₇) membered cycloalkyl, substituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl.

[0069] In a related embodiment, each substituted alkylene, substituted heteroalkylene, substituted cycloalkylene, substituted heterocycloalkylene, substituted arylene, and

substituted heteroarylene described herein as possible R moieties are substituted only with at least one substituent independently selected from -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted 2 to 5 membered heteroalkyl, unsubstituted (C₃-C₇) membered cycloalkyl, unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl. In another related embodiment, each substituted alkylene, substituted heteroalkylene, substituted cycloalkylene, substituted heterocycloalkylene, substituted arylene, and substituted heteroarylene described herein as possible R moieties are substituted only with at least one substituent independently selected from -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted (C₃-C₇) membered cycloalkyl, and unsubstituted phenyl. In yet another related embodiment, each substituted alkylene, substituted heteroalkylene, substituted cycloalkylene, substituted heterocycloalkylene, substituted arylene, and substituted heteroarylene described herein as possible R moieties are substituted only with at least one unsubstituted (C₁-C₃)alkyl.

[0070] A may be selected from -OR⁴, substituted or unsubstituted (C₁-C₁₀)alkyl, substituted or unsubstituted 2 to 12 membered heteroalkyl, substituted or unsubstituted (C₃-C₇)cycloalkyl, substituted or unsubstituted 5 to 7 membered heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl. R⁴ may be selected from hydrogen, substituted or unsubstituted (C₁-C₁₀)alkyl, substituted or unsubstituted 2 to 10 membered heteroalkyl, substituted or unsubstituted (C₃-C₇)cycloalkyl, substituted or unsubstituted 5 to 7 membered heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl.

[0071] In some embodiments, A is selected from -OR⁴, unsubstituted (C₁-C₁₀)alkyl, unsubstituted 2 to 12 membered heteroalkyl, unsubstituted (C₃-C₇)cycloalkyl, unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl. In a related embodiment, A is selected from -OR⁴, unsubstituted (C₁-C₁₀)alkyl, unsubstituted 3 to 12 membered alkylether, unsubstituted (C₃-C₇)cycloalkyl, and unsubstituted phenyl.

[0072] A may also be selected from -OR⁴, unsubstituted (C₁-C₄)alkyl, unsubstituted 3 to 8 membered alkylether, unsubstituted (C₃-C₇)cycloalkyl, and unsubstituted phenyl. Alternatively, A is selected from -OR⁴, unsubstituted (C₁-C₄)alkyl, and unsubstituted 3 to 8 membered alkylether.

[0073] R^4 may be selected from hydrogen, unsubstituted (C_1 - C_{10})alkyl, unsubstituted 2 to 12 membered heteroalkyl, unsubstituted (C_5 - C_7)cycloalkyl, unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl.

[0074] In some embodiments, R^4 is selected from hydrogen, unsubstituted (C_1 - C_{10})alkyl, unsubstituted 3 to 12 membered alkylether, unsubstituted (C_5 - C_7)cycloalkyl, and unsubstituted phenyl. In a related embodiment, R^4 is selected from hydrogen, unsubstituted (C_1 - C_8)alkyl, unsubstituted 3 to 8 membered alkylether, unsubstituted (C_5 - C_7)cycloalkyl, and unsubstituted phenyl. Alternatively, R^4 is selected from hydrogen, unsubstituted (C_1 - C_8)alkyl, and unsubstituted 3 to 8 membered alkylether.

[0075] R^4 may also be selected from phenyl, methylphenyl, substituted or unsubstituted (C_1 - C_8)alkyl, and $-(CH_2)_x-O-(CH_2)_yCH_3$. x and y are integers independently selected from 1 to 10.

[0076] R may be selected from substituted or unsubstituted (C_1 - C_{10}) alkylene, substituted or unsubstituted 2 to 10 membered heteroalkylene, substituted or unsubstituted (C_5 - C_7)cycloalkylene, substituted or unsubstituted 2 to 7 membered heterocycloalkylene, substituted or unsubstituted arylene, and substituted or unsubstituted heteroarylene.

[0077] In an exemplary embodiment, R is a member selected from unsubstituted (C_1 - C_{10})alkylene, unsubstituted 2 to 10 membered heteroalkylene, unsubstituted (C_5 - C_7)cycloalkylene, unsubstituted 5 to 7 membered heterocycloalkylene, unsubstituted arylene, and unsubstituted heteroarylene.

[0078] R may also be unsubstituted (C_1 - C_{10})alkylene.

[0079] R^1 , R^2 , and R^3 may be selected from hydrogen, substituted or unsubstituted (C_1 - C_{20})alkyl, substituted or unsubstituted 2 to 20 membered heteroalkyl, substituted or unsubstituted (C_5 - C_7)cycloalkyl, substituted or unsubstituted 5 to 7 membered heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl.

[0080] In some embodiments, R^1 , R^2 , and R^3 are independently selected from hydrogen, unsubstituted (C_1 - C_{20})alkyl, hydroxy-substituted (C_1 - C_{20})alkyl, amine-substituted (C_1 - C_{20})alkyl, unsubstituted 2 to 20 membered heteroalkyl, unsubstituted (C_5 - C_7)cycloalkyl, unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl. In a related embodiment, R^1 , R^2 , and R^3 are independently selected from

hydrogen, unsubstituted (C₁-C₂₀)alkyl, unsubstituted alkylether, hydroxy-substituted (C₁-C₂₀)alkyl, amine-substituted (C₁-C₂₀)alkyl, unsubstituted (C₅-C₇)cycloalkyl, and unsubstituted phenyl.

[0081] R¹, R², and R³ may also be selected from hydrogen, unsubstituted (C₁-C₂₀)alkyl, unsubstituted alkylether, hydroxy-substituted (C₁-C₂₀)alkyl, amine-substituted (C₁-C₂₀)alkyl, unsubstituted (C₅-C₇)cycloalkyl, and unsubstituted phenyl. Alternatively, R¹, R², and R³ is selected from hydrogen, unsubstituted (C₁-C₂₀)alkyl, unsubstituted alkylether, hydroxy-substituted (C₁-C₂₀)alkyl, and amine-substituted (C₁-C₂₀)alkyl.

[0082] In other exemplary embodiments, R¹, R², and R³ are independently selected from -(CH₂)_qOCH₃, -(CH₂)_qOH, -(CH₂)_qO(CH₂)_tCH₃, -(CH₂)_qNHCH₃, -(CH₂)_qNH₂, -(CH₂)_qN(CH₃)₂ and -(CH₂)_qNH₂(CH₂)_tCH₃, in which q and t are integers independently selected from 0 to 10. R¹, R², and R³ may also members independently selected from the group consisting of -CH₂CH₂OCH₃ and -CH₂CH₂OCH₂CH₂CH₃. Alternatively, R¹, R², and R³ may also be independently selected from -CH₂CH₂OH and -CH₂CH₂CH₂CH(OH)CH₃. R¹, R², and R³ may also be independently selected from -CH₂CH₂NH₂ and -CH₂CH₂N(CH₃)₂. Finally, R¹, R², and R³ may be members independently selected from methyl, octadecyl, didecyl, and tetracecyl.

[0083] In an exemplary embodiment, the quaternary ammonium organosilane reagent is selected from (CH₃O)₃Si(CH₂)₃N⁺(CH₃)₂(C₁₈H₃₇) (Cl⁻); (CH₃CH₂O)₃Si(CH₂)₃N⁺(CH₃)₂(C₁₈H₃₇) (Cl⁻); (CH₃O)₃Si(CH₂)₃N⁺(CH₃)₂(C₁₈H₃₇) (Br⁻); (CH₃O)₃Si(CH₂)₃N⁺(C₁₀H₂₁)₂(CH₃) (Cl⁻); (CH₃O)₃Si(CH₂)₃N⁺(CH₃)₂(C₁₄H₂₉) (Cl⁻); (CH₃O)₃Si(CH₂)₃N⁺(CH₃)₂(C₁₄H₂₉) (Br⁻); and (CH₃O)₃Si(CH₂)₃N⁺(CH₃)₂(C₁₆H₃₃) (Cl⁻). In a related embodiment, the quaternary ammonium organosilane reagent is selected from 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride, 3-(trimethoxysilyl)propyldidecylmethyl ammonium chloride, and 3-(trimethoxysilyl)propyldimethyltetradecyl ammonium chloride.

[0084] In another exemplary embodiment, the quaternary ammonium organosilane contains an ammonium halide and a hydrolyzable alkoxy group bonded to silicon.

Quaternary Ammonium Organosilane Coatings

[0085] A variety of methods may be used to form the quaternary ammonium organosilane coatings from quaternary ammonium organosilane reagents. The quaternary ammonium

organosilane reagent may be applied to the solid phase carrier using any method known in the art, including, for example, methods for covalently or non-covalently binding the quaternary ammonium organosilane reagent to the solid phase carrier to form a quaternary ammonium organosilane coating.

[0086] Solid phase carriers may be contacted (e.g. sprayed, dipped, or otherwise applied) with a solution preparation containing the quaternary ammonium organosilane reagent. In some embodiments, the quaternary ammonium organosilane reagent coated surfaces are allowed to air dry at room temperatures for a sufficient period of time to complete a condensation cure of the quaternary ammonium organosilane coating. Alternatively, heat is applied to the coated surfaces for a sufficient period of time to effect cure, the duration and temperature of such is known to those skilled in the art.

[0087] In an exemplary embodiment, the quaternary ammonium organosilane reagent is covalently bound to the solid phase carrier. Typically, the quaternary ammonium organosilane reagent is covalently bound to an accessible carrier reactive group that forms a part of the solid phase carrier. A variety of reactive groups are useful in covalently binding the quaternary ammonium organosilane reagent. The quaternary ammonium organosilane reagent may be covalently bound to the carrier reactive group through the silane moiety of the quaternary ammonium organosilane reagent. The silane moiety, as used herein, refers to the A_{4-n} -Si- portion of the compound of Formula (I).

[0088] The silane moiety may be covalently bound to the carrier reactive group by allowing the carrier reactive group to covalently bind to the silicon atom of the silane moiety. For example, where the carrier reactive group is a hydroxyl, the oxygen atom may be allowed to bind to the silicon atom to form a silicon-oxygen bond thereby covalently attaching the quaternary ammonium organosilane reagent to the carrier molecule. In a related embodiment, the silane moiety includes at least one $-OR^4$ that leaves upon attack of a hydroxyl carrier reactive group. This reaction may be referred to herein as a condensation reaction. Thus, the quaternary ammonium organosilane reagent may be covalently attached to the carrier molecule via a condensation reaction.

[0089] The silane moiety may also include an A group that contains a reactive group, referred to herein as a silane reactive group. The silane reactive group is capable of reacting with a carrier reactive group to form a covalent bond.

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[0090] Silane reactive groups, carrier reactive groups and classes of reactions useful in covalently attaching quaternary ammonium organosilane reagents to a solid phase carrier are generally those that are well known in the art of bioconjugate chemistry. These include, but are not limited to nucleophilic substitutions (*e.g.*, reactions of amines and alcohols with acyl halides, active esters), electrophilic substitutions (*e.g.*, enamine reactions) and additions to carbon-carbon and carbon-heteroatom multiple bonds (*e.g.*, Michael reaction, Diels-Alder addition). These and other useful reactions are discussed in, for example, March, **ADVANCED ORGANIC CHEMISTRY**, 3rd Ed., John Wiley & Sons, New York, 1985; Hermanson, **BIOCONJUGATE TECHNIQUES**, Academic Press, San Diego, 1996; and Feeney *et al.*, **MODIFICATION OF PROTEINS**; *Advances in Chemistry Series*, Vol. 198, American Chemical Society, Washington, D.C., 1982.

[0091] Useful silane and carrier reactive functional groups include, for example:

[0092] (a) carboxyl groups and various derivatives thereof including, but not limited to, N-hydroxysuccinimide esters, N-hydroxybenztriazole esters, acid halides, acyl imidazoles, thioesters, p-nitrophenyl esters, alkyl, alkenyl, alkynyl and aromatic esters;

[0093] (b) hydroxyl groups which can be converted to esters, ethers, aldehydes, *etc.*

[0094] (c) haloalkyl groups wherein the halide can be later displaced with a nucleophilic group such as, for example, an amine, a carboxylate anion, thiol anion, carbanion, or an alkoxide ion, thereby resulting in the covalent attachment of a new group at the site of the halogen atom;

[0095] (d) dienophile groups which are capable of participating in Diels-Alder reactions such as, for example, maleimido groups;

[0096] (e) aldehyde or ketone groups such that subsequent derivatization is possible via formation of carbonyl derivatives such as, for example, imines, hydrazones, semicarbazones or oximes, or via such mechanisms as Grignard addition or alkyllithium addition;

[0097] (f) sulfonyl halide groups for subsequent reaction with amines, for example, to form sulfonamides;

[0098] (g) thiol groups, which can be converted to disulfides or reacted with acyl halides;

[0099] (h) amine or sulfhydryl groups, which can be, for example, acylated, alkylated or oxidized;

[0100] (i) alkenes, which can undergo, for example, cycloadditions, acylation, Michael addition, *etc.*;

[0101] (j) epoxides, which can react with, for example, amines and hydroxyl compounds; and

[0102] (k) phosphoramidites and other standard functional groups useful in nucleic acid synthesis.

[0103] The reactive functional groups can be chosen such that they do not participate in, or interfere with, the reactions necessary to assemble the quaternary ammonium organosilane coating. Alternatively, a silane or carrier reactive functional group can be protected from participating in the reaction by the presence of a protecting group. Those of skill in the art will understand how to protect a particular functional group from interfering with a chosen set of reaction conditions. For examples of useful protecting groups, *See Greene et al.*, **PROTECTIVE GROUPS IN ORGANIC SYNTHESIS**, John Wiley & Sons, New York, 1991.

[0104] Linkers may also be employed to attach the quaternary ammonium organosilane reagent to the solid phase carrier. Linkers may include reactive groups at the point of attachment to the quaternary ammonium organosilane reagent and/or the solid phase carrier. Any appropriate linker may be used in the present invention, including substituted or unsubstituted alkylene, substituted or unsubstituted heteroalkylene, substituted or unsubstituted cycloalkylene, substituted or unsubstituted heterocycloalkylene, substituted or unsubstituted arylene, and substituted or unsubstituted heteroarylene. In an exemplary embodiment, the linker group is selected from substituted or unsubstituted alkylene, and substituted or unsubstituted heteroalkylene. In a related embodiment, the linker is selected from unsubstituted alkylene, alkylene substituted with at least one oxy, unsubstituted heteroalkylene, and heteroalkylene substituted with at least one oxy. In another related embodiment, the linker is selected from unsubstituted (C₁-C₂₅) alkylene, (C₁-C₂₅) alkylene substituted with at least one oxy, unsubstituted 2 to 26 membered heteroalkylene, and 2 to 26 membered heteroalkylene substituted with at least one oxy.

[0105] Other useful linkers include those having a polyester backbone (e.g. polyethylene glycol), and derivatives thereof. A wide variety of useful linkers are commercially available (e.g. polyethylene glycol based linkers such as those available from Nektar, Inc. of Huntsville, Alabama).

[0106] The quaternary ammonium organosilane reagent may also be non-covalently attached to the solid phase carrier using any interaction, such as Van der Waals interactions, hydrophobic interactions, dipole-dipole interactions, electrostatic interactions, and/or hydrogen bonding interactions.

[0107] In an exemplary embodiment, the quaternary ammonium organosilane reagent forms a polymeric network that partially or wholly covers the solid phase carrier. Where the quaternary ammonium organosilane reagent forms a polymeric network, the quaternary ammonium organosilane reagent may additionally form a covalent and/or non-covalent bond with the solid phase carrier.

[0108] The quaternary ammonium organosilane reagent typically forms a polymeric network by covalently binding through the silane moiety. Where the silane moiety includes at least one $-OR^4$ group, the quaternary ammonium organosilane reagent may form a silicone polymer having a series of silicon-oxygen-silicon bonds. The silicones may be linear polymers or cross-linked polymers. For example, where the silane moiety includes at least two $-OR^4$ groups, the quaternary ammonium organosilane reagent may form a cross-linked silicone polymer wherein each silica atom forms part of at least two silicon-oxygen-silicon bonds. Thus, polymerization may be achieved using silane reactive groups capable of forming intermolecular covalent bonds with other silane reactive groups.

[0109] In an exemplary embodiment, the quaternary ammonium organosilane reagent is contacted with an aqueous liquid prior to application to the solid phase carrier. As discussed above, useful quaternary ammonium organosilane reagents include those containing hydrolyzable alkoxy groups bound to the silicon atom. Upon contact with a water molecule, the alkoxy groups (e.g. methoxy) may hydrolyze to form hydroxy substituted silicon atoms (also referred to herein as "silanols") with simultaneous liberation of alcohol as a by-product of the hydrolysis (also referred to herein as condensation). The resultant compound formed on addition of quaternary ammonium organosilanes of the above compositions are the corresponding mono-, di-, or tri-silanol species. The reactive silanol species prepared upon hydrolysis may form covalent silicon-oxygen-silicon bonds with other silanol species resulting in polymeric coatings as described above. The resultant polymeric coating may be a molecular network non-covalently and/or covalently bonded to the solid phase carrier.

[0110] It will be understood by those skilled in the art that the quaternary ammonium organosilane coating may form three dimensional, cross-linked, water-insoluble, polymeric

coatings which may contain some uncondensed silanol or alkoxy moieties. Monomeric, dimeric and oligomeric species may be present on the solid phase carrier following application of an aqueous solution containing quaternary ammonium organosilane reagent, and these may bond to the solid phase carrier, whether by covalent or non-covalent mechanisms.

[0111] The quaternary ammonium organosilane coatings formed on the solid phase carriers retain their antimicrobial activity. They are substantive to the solid phase carriers and largely insoluble in aqueous liquid. For example, in some embodiments, less than 10 ppb of quaternary ammonium organosilane reagents is detectable in water after Standard 42 testing as performed by NSF International, Ann Arbor, MI.

[0112] In an exemplary embodiment, the quaternary ammonium organosilane coating has the formula:



[0113] In Formula (II), A, R, R¹, R², and R³ are as defined above in Formula (I). W is a solid phase carrier as described above. The solid phase carrier W may include a linker moiety and/or the remnant of a reactive group. The symbol l represents an integer selected from 1, 2, or 3. The symbols m and j represent integers independently selected from 0, 1, 2, and 3, wherein both m and j are not simultaneously 0. The sum of m, j, and l is not greater than four. In a related embodiment, l is 1, 2, or 3; m is 1, 2, or 3, and j is 1, 2, or 3. In another related embodiment, l is 1; m is 1, 2, or 3, and j is 1, 2, or 3.

Microorganisms

[0114] The term "microorganism," as used herein, means an organism that, individually, can only be seen through a microscope. The term microorganism includes, for example, bacteria, fungi, actinomycetes, algae, protozoa, yeast, germs, ground pearls, nematodes, viruses, prions, and algae. Thus, in an exemplary embodiment, the microorganism is selected from bacteria, viruses (also referred to herein as bacteriophages), fungi, algae, mold, yeast, spores, and protozoa parasites. The term "bacteria" includes both gram positive and gram negative bacteria.

[0115] Gram positive bacteria include, for example, *Bacillus sp.* (vegetative cell), *Corynebacterium diphtheriae*, *Micrococcus lutea*, *Micrococcus sp.*, *Mycobacterium tuberculosis*, *Mycobacterium smegmatis*, *Propionibacterium acnes*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Streptococcus faecalis*, *Streptococcus mutans*, *Streptococcus pneumonia*, and *Streptococcus pyogenes*.

[0116] Gram negative bacteria include, for example, *Acinetobacter calcoaceticus*, *Aeromonas hydrophilia*, *Citrobacter deversus*, *Citrobacter freundii*, *Enterobacter aerogenes*, *Enterobacter agglomerans*, *Escherichia coli*, *Klebsiella oxytoca*, *Klebsiella pneumoniae*, *Klebsiella terrigena*, *Legionella pneumophila*, *Morganella morganii*, *Proteus mirabilis*, *Proteus vulgaris*, *Pseudomonas aeruginosa*, *Pseudomonas fluorescens*, *Salmonella cholerae* suts, *Salmonella typhi*, *Salmonella typhimurium*, *Serratia liquefaciens*, and *Xanthomonas campestris*.

[0117] Viruses include, for example, Adenovirus Type II & IV, Bovine Adenovirus Type I & IV, Feline pneumonitis, Herpes Simplex Type I, Herpes Simplex Type II, HIV-1 (AIDS), Influenza A2 (Aichi), Influenza A2 (Asian), Influenza B, Mumps, Parainfluenza (Sendai), Reovirus Type I, Simian Virus 40, Vaccinia, MS2, and PRD1.

[0118] Fungi, algae, mold, yeast, and spores include, for example, *Alteraria alternata*, *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus sydowii*, *Aspergillus terreus*, *Aspergillus versicolor*, *Aspergillus verrucaria*, *Aureobasidium pullans*, *Candida albicans*, *Candida pseudotropicalis*, *Chaetomium globosum*, *Cladosporium cladosporioides*, *Chlorella vulgaris*, *Dreschlera australiensis*, *Epidermophyton sp.*, *Gliomastix cerealis*, *Gloeophyllum trabeum*, *Microsporum sp.*, *Microsporum audouinii*, *Monilia grisea*, *Oscillatoria*, *Penicillium chrysogenum*, *Penicillium commune*, *Penicillium funiculosum*, *Penicillium pinophilum*, *Penicillium variable*, *Phoma fimeii*, *Pithomyces chartarum*, *Poria placenta*, *Scenedesmus*, *Saccharomyces cerevisiae*, *Sclerotinia sclerotiorum*, *Sclerotinia sclerotiorum*, *Trichoderma viride*, *Trichophyton interdigitale*, *Trichophyton maidson*, *Trichophyton mentagrophytes*, and *Trichophyton sp.*

[0119] Protozoa parasites include, for example, *Cryptosporidium parvum* (oocysts) and *Giardia*.

[0120] For more detailed information regarding antimicrobial activity against gram positive bacteria, gram negative bacteria, viruses, fungi, algae, mold, yeast, spores and protozoa parasites, see Hsiao, Y. Chinese Pat. Appl., PCT/CN98/00207 (1998); Malek, J. et al., U.S. Pat. 4,259,103 (1981); Klein, S., U.S. Pat. 4,394,378 (1983); Eudy, W., U.S. Pat. 4,406,892

(1983); Gettings, R. et al., U.S. Pat. 4,908,355 (1990) and U.S. Pat. 5,013,459 (1991); Blank, L. et al., U.S. Pat. 5,145,596 (1992); Avery, R. U.S. Pat. 5,411,585 (1995); Blank, L. et al., U.S. Pat. 4,865,844 (1989); Battice, D. et al., U.S. Pat. 4,631,297 (1986); Higgs, B. et al., U.S. Pat. 5,359,104 (1994); Avery, R et al., U.S. Pat. 5,411,585 (1995); White, W. et al., *Book of Papers, 12th Annual Nonwovens Tech. Symposium*, pp. 13-46 (1984); McGee, J. et al., *Am. Dyestuff Rep.* 6: 56-59 (1983); Dow Corning Technical Brochure; 22-994-83 (1983); Gettings, R. et al., *Book of Papers, American Association of Textile Chemists and Colorists National Technical Conference*, pp. 259-261 (1978); Dow Corning Technical Brochure, 24-095-85 (1985); Tsao, I et al., *Biotechnol. Bioeng.*, 34: 639-46 (1989); Tsao, I et al., *ACS Symp.Ser.* 419: 250-67 (1990); Klein, M. et al., *Principles of Viral Inactivation*, 3rd Ed., S. Block, Ed., (Lea & Febiger, Philadelphia, PA) pp.422-434 (1983); Peterson, W. et al., U. S. Patent 6,613,755; each of which is incorporated by reference in their entirety for all purposes.

[0121] The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding equivalents of the features shown and described, or portions thereof, it being recognized that various modifications are possible within the scope of the invention claimed. Moreover, any one or more features of any embodiment of the invention may be combined with any one or more other features of any other embodiment of the invention, without departing from the scope of the invention. For example, the features of the reagents of the present invention are equally applicable the coatings of the present invention described herein. All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entirety for all purposes.

Examples

[0122] The following examples are provided by way of illustration only and not by way of limitation. Those of skill in the art will readily recognize a variety of non-critical parameters that can be changed or modified to yield similar results.

[0123] ODTA: Octadecyldimethyl(3-trimethoxysilyl)propyl ammonium chloride. Obtained from Wright Chemical Corp., Wilmington, NC as a 42% active material in methanol. This material may also be named as 3-(trimethoxysilyl)propyl-dimethyloctadecyl

ammonium chloride. Also available as a 42% active material from Aegis Environmental Management, Inc., Midland, MI marketed as Dow Corning® 5700.

[0124] REQUAT: 3-(trimethoxysilyl)propyldidecylmethyl ammonium chloride. Obtained from Sanitized Inc., New Preston, CT; Requat 1977 as a 42% active material in methanol.

[0125] TDTA: 3-(trimethoxysilyl)propyltetradecyldimethyl ammonium chloride obtained from Gelest, Inc., Tullytown, PA, Cat. No. SIT7090.0 as a 50% solution in methanol.

EXAMPLE 1.

[0126] A solution suitable for application was prepared by adding 4 parts ODTA to 100 parts deionized water with stirring. The resulting clear solution was applied to an open, polyvinyl chloride (PVC) flat-type evaporation pan by atomized spray, insuring that all surfaces were thoroughly wetted. The pan is allowed to air dry for 24 hours to cure the quaternary ammonium organosilane reagents to the container surface to form a quaternary ammonium organosilane coating. Water containing bacteria level previously measured at 10^7 total bacteria/ml using a BIOSPERSE® Test Kit was added to the pan in a ratio of 4.6 grams of water per square inch of surface area. After 30 minutes the water is sampled using a BIOSPERSE® test kit. After incubation, 10^5 bacteria/ml was measured. Resampling of the test water at 1 hour and 4 hours gave bacterial counts of 10^4 and $<10^3$, respectively.

EXAMPLE 2.

[0127] A 4 oz. solution prepared according to Example 1 was added to a 1 pint tin-plated metal test container having 3/4 inch screw top. The solution was agitated to completely wet the inside surface of the container for 1 minute and then decanted. The test container was allowed to air dry for one hour. Residual vapors were removed by an air purge for 5 minutes and the container was then heated to 105 °C for one hour to cure the quaternary ammonium organosilane reagents to the container surface to form a quaternary ammonium organosilane coating. Water (300 g) having a high bacterial count of 10^7 bacteria/ml was added to the test container. The test container was allowed to stand one hour at room temperature. After two hours, the test water bacterial level was measured at 10^3 bacteria/ml using a BIOSPERSE® test kit.

EXAMPLE 3.

[0128] Two ounce containers of glass, high density polyethylene (HDPE), polypropylene (PP) or polyvinyl chloride (PVC) were treated with an aqueous solution containing 1.5% TDTA. The containers were heated to 100 °C for one hour to cure the quaternary ammonium organosilane reagent to the container surfaces to form a quaternary ammonium organosilane coating. Each container was then rinsed with one oz. of deionized water. One ounce of water containing 10^3 bacteria/ml was added to each containers and capped. After 24 hours at room temperature, each container was sampled and bacteria measured with a BIOSPERSE® test kit. All containers indicated bacteria counts of 10^3 bacteria/ml following incubation for 24 hours.

EXAMPLE 4.

[0129] Coiled aluminum test tubing 8 ft. in length and having an internal diameter of 1/4 inch was treated with a solution of 8 parts REQUAT to 100 parts isopropanol. The tube was filled with the solution, sealed and allowed to stand for 15 minutes. The tube was drained and air dried with a stream of compressed air passing through the tube at a rate of 100 ml/minute for 24 hours to cure the quaternary ammonium organosilane reagent to the tubing surfaces to form a quaternary ammonium organosilane coating. An aqueous liquid containing 10^7 units/ml of bacteria and algae was passed through the coiled aluminum tubing. The aqueous liquid was gravity circulated through the tubing at a rate of 5 ml/minute resulting in contamination of $<10^3$ bacteria/ml.

EXAMPLE 5.

[0130] An antimicrobial solution suitable for treatment of siliceous surfaces including sand and zeolites was prepared by adding 67.5 grams REQUAT to a stirred solution containing 3.375 kg deionized water and 3 grams of 3-aminopropyltrimethoxysilane. One kg of the clear solution was sprayed onto 50 pounds of #20 white silica pool filter sand over 5 minutes in a rotary mixer. The wetted material was mixed with agitation for an additional hour and allowed to air dry 24 hrs to cure the quaternary ammonium organosilane reagent to the sand surface to form a quaternary ammonium organosilane coating. The treated sand was employed in a recirculating water system to reduce microbial contamination from 10^7 bacteria/ml to $<10^3$ bacteria/ml in 30 minutes of operation as measured by a BIOSPERSE® test kit.

EXAMPLE 6.

[0131] Zeolites containing approximately 90% clinoptilolite (Ash Meadows Zeolites, LLC) of 20-40 mesh were thoroughly wetted with a solution containing 7 parts ODTA and 93 parts water. The wet zeolites were allowed to air dry 24 hours and then heated 2 hours at 110 °C in a forced air oven to cure the quaternary ammonium organosilane reagent to the zeolite surfaces to form a quaternary ammonium organosilane coating. The treated zeolites were placed in a 2 inch PVC pipe having an overall length of 38 inches. As described below, dechlorinated water containing known quantities of bacteriophages, bacteria, algae and protozoa were passed through the PVC pipe containing the quaternary ammonium organosilane coated zeolites.

[0132] The experimental apparatus consisted of a set of three filters (filter 1, 2 and 3) attached to a manifold, which included fittings for hose connections, and sample ports at the inlet and outlet for each filter (see FIG. 6). An inline mixer was included in the pipe assembly before inlet port to maximize microbial monodispersity. The challenge test water was pumped into each filter at a flow rate of 330 ml/min using a thermally protected pump.

[0133] Prior to each microbial challenge, the filters were flushed for 25 minutes with dechlorinated tap water. The flush water was dechlorinated using granular activated carbon filter and chlorine residual was measured before and after the dechlorination using Hach method 8167.

[0134] The challenge test water was prepared by adding known number of microorganisms into 20 liters of dechlorinated tap water in a polypropylene container (Nalgene, Rochester, NY). Microbes were washed with 1X phosphate buffered saline just before spiking in the container. The challenge test water container was placed on a stir plate with a Teflon coated stir bar and continuously mixed to provide homogenous distribution of microbes in the influent water. The challenge test water was pumped into each filter using a thermally protected pump (Little Giant Potent Pump, Oklahoma City, OK). The pump was primed prior to use by recirculating the microbial stock solution. The hose was connected to the inlet fitting of each filter. The pump was operated for twelve minutes for each filter. The flow rate was measure using a 1000 ml graduated cylinder and adjusted to 330 ml/min as recommended by CSL. Based on the hydraulic parameters of the system, each filter needed a 12-minute-run to stabilize. The effluent samples were taken from each filter after twelve minutes and a single influent sample was collected from the second filter after eight minutes,

which represented influent concentration for the complete run. Once the experiment was complete, the filters were again flushed for 30 minutes with dechlorinated tap water.

6.1 Bacteriophages

[0135] A series of experiments were conducted with the bacteriophages MS2 and PRD1. The effluent and influent samples were taken and diluted as described above. The samples for MS2 and PRD1 were serially diluted and assayed using their respective bacterial hosts by double layer agar method (Adams, M.H., *Bacteriophages*, Interscience, New York (1959)). The plates were incubated at 37°C for 24 hours, at which time clear virus plaques were counted. The results are presented in FIG. 1. The log removal and inactivation for MS2 and PRD1 ranged between 2.40 to 2.96, and 1.50 to 2.27 log, respectively. The over average removal for MS2 and PRD1 were 2.8 and 2.0 log, respectively. The data shows that quaternary ammonium organosilane coated zeolite can reduce the viable number of bacteriophages in aqueous liquid.

6.2 Bacteria

[0136] An independent series of experiments were conducted with the bacteria *Klebsiella terrigena* and *E. Coli* (ATCC 25922). The effluent and influent samples were taken and diluted as described above. The samples were assayed by membrane filtration techniques using 0.4 µm pore size membrane filter. The membrane filter was placed on a selective medium and incubated at 37°C for 24 hours, at which time bacterial colonies were counted. The results are presented in FIG. 2(A) and (B). As shown in FIG. 2(A) and FIG. 3, consistent removal for *Klebsiella* was observed in all the filters, which ranged from 99.37% (2.2 log) to 99.60% (2.4 log) with an average of 99.50% (2.3 log). As shown in FIG. 2(B), the removal for *E. coli* ranged from 99.96% (3.50 log) to 99.99% (4.39 log) with an average of 99.98% (3.88 log). This study shows that quaternary ammonium organosilane coated zeolite can effectively reduce the viable number bacteria in aqueous liquid.

6.3 Algae

[0137] Experiments were conducted with *Chorella vulgaris* to determine both the removal as well as inactivation effects of the media against algae. The effluent and influent samples were taken and diluted as described above. The samples were concentrated by centrifugation before assaying for total removal and inactivation. Removal was determined by total volumetric counts under microscope. The inactivation rate was determined by viability test.

The algal cells were digested with 2% trypsin (in hanks balanced salt solution) and stained with Fluorescein Diacetate (Sigma Chemicals F-7378). Fluorescein Diacetate (FDA) is a non-polar ester that passes through cell membranes. Once inside the cell, FDA is hydrolyzed by esterases (an enzyme present in viable cells) to produce fluorescein, which accumulates inside viable cell walls and fluoresce under UV light. A microscope equipped with both white and ultraviolet light, was used to quantify live and dead algal cells. The results are presented in FIG. 4. The average removal of 99.11% (2.05 log), 98.74% (1.90 log) and 98.74% (1.90 log) were observed for filter 1, 2, and 3, respectively. The average of three inactivation measurements for filter 1, 2, and 3 were 11% (0.05%), 12% (0.06 log) and 22% (0.11 log), respectively. However, based on individual measurements the over all range of inactivation for the three filters was 5% (0.02 log) to 46% (0.27 log) and averaged at 15% (0.07 log). It is clear that quaternary ammonium organosilane coated zeolite can effectively reduce the viable number algae in aqueous liquid.

6.4 Protozoa Parasites

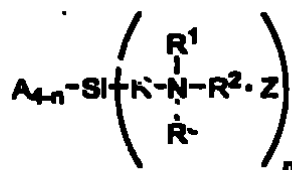
[0138] *Cryptosporidium parvum* oocysts were obtained from the Sterling Parasitology Laboratory at the University of Arizona, Tucson, Arizona, and were used to determine the efficacy of removal or inactivation of infectious oocysts. The removal of *Cryptosporidium parvum* oocysts was determined by Hemacytometer counts on concentrated samples, whereas, the number of infectious oocysts were determined by infection foci detection method using cell culture technique with the most-probable-number assay (FDM-MPN) (Slifko et al., *Applied Environmental Microbiology*, 65:3936-3941 (1999)). The results are presented in FIG. 5.

[0139] The cumulative removal/inactivation of infectious *C. parvum* oocysts averaged at 97.9% (1.68 log) for all three filters. The removal and inactivation performance by each filter were 95.4% (1.34 log), 99.3% (2.15 log), and 98.9% (1.96 log) for filters 1, 2, and 3, respectively. The removal (only) of oocysts averaged at 71.3% (0.54 log) with an individual removal of 75.9% (0.62 log), 65.5% (0.46 log), and 72.4% (0.56) for filters 1, 2, and 3, respectively. The study indicates that quaternary ammonium organosilane coated zeolite can effectively reduce the viable number protozoa parasites in aqueous liquid.

WHAT IS CLAIMED IS:

1 1. A method of reducing or eliminating the viable number of
2 microorganisms in a liquid, said method comprising contacting said liquid with a solid
3 phase carrier coated with a quaternary ammonium organosilane coating.

1 2. A method in accordance with claim 1 in which said quaternary
2 organosilane coating is produced from a quaternary ammonium organosilane reagent
3 having the formula:



4
5 wherein:

6 A is a member independently selected from the group consisting of -OR⁴,
7 substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl,
8 substituted or unsubstituted cycloalkyl, substituted or unsubstituted
9 heterocycloalkyl, substituted or unsubstituted aryl, and substituted or
10 unsubstituted heteroaryl,

11 wherein R⁴ is a member selected from the group consisting of hydrogen,
12 substituted or unsubstituted alkyl, substituted or unsubstituted
13 heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or
14 unsubstituted heterocycloalkyl, substituted or unsubstituted aryl,
15 and substituted or unsubstituted heteroaryl;

16 R is a member selected from the group consisting of substituted or unsubstituted
17 alkylene, substituted or unsubstituted heteroalkylene, substituted or
18 unsubstituted cycloalkylene, substituted or unsubstituted
19 heterocycloalkylene, substituted or unsubstituted arylene, and substituted
20 or unsubstituted heteroarylene;

21 R¹, R², and R³ are members independently selected from the group consisting of
22 hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted
23 heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or
24 unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and
25 substituted or unsubstituted heteroaryl;

26 Z is a member selected from the group consisting of fluoride, chloride, bromide,
27 iodide, tosylate, hydroxide, sulfate and phosphate; and
28 n is 1, 2 or 3.

1 3. A method in accordance with claim 1 in which
2 A is a member independently selected from the group consisting of -OR⁴,
3 substituted or unsubstituted (C₁-C₁₀)alkyl, substituted or unsubstituted 2 to
4 10 membered heteroalkyl, substituted or unsubstituted (C₃-C₇)cycloalkyl,
5 substituted or unsubstituted 5 to 7 membered heterocycloalkyl, substituted
6 or unsubstituted aryl, and substituted or unsubstituted heteroaryl;
7 wherein R⁴ is a member selected from the group consisting of hydrogen,
8 substituted or unsubstituted (C₁-C₁₀)alkyl, substituted or
9 unsubstituted 2 to 10 membered heteroalkyl, substituted or
10 unsubstituted (C₃-C₇)cycloalkyl, substituted or unsubstituted 5 to 7
11 membered heterocycloalkyl, substituted or unsubstituted aryl, and
12 substituted or unsubstituted heteroaryl;
13 R is a member selected from the group consisting of substituted or unsubstituted
14 (C₁-C₁₀) alkylene, substituted or unsubstituted 2 to 10 membered
15 heteroalkylene, substituted or unsubstituted (C₃-C₇)cycloalkylene,
16 substituted or unsubstituted 5 to 7 membered heterocycloalkylene,
17 substituted or unsubstituted arylene, and substituted or unsubstituted
18 heteroarylene; and
19 R¹, R², and R³ are members independently selected from the group consisting of
20 hydrogen, substituted or unsubstituted (C₁-C₂₀)alkyl, substituted or
21 unsubstituted 2 to 20 membered heteroalkyl, substituted or unsubstituted
22 (C₃-C₇)cycloalkyl, substituted or unsubstituted 5 to 7 membered
23 heterocycloalkyl, substituted or unsubstituted aryl, and substituted or
24 unsubstituted heteroaryl.

1 4. A method in accordance with claim 3 in which
2 each substituted alkyl, substituted heteroalkyl, substituted cycloalkyl, substituted
3 heterocycloalkyl, substituted aryl, and substituted heteroaryl are
4 substituted only with at least one substituent independently selected from
5 the group consisting of -OH, unsubstituted (C₁-C₅)alkyl, unsubstituted 2 to

6 5 membered heteroalkyl, unsubstituted (C₅-C₇) membered cycloalkyl,
7 unsubstituted 5 to 7 membered heterocycloalkyl, unsubstituted aryl, and
8 unsubstituted heteroaryl; and

9 said substituted alkylene, substituted heteroalkylene, substituted cycloalkylene,
10 substituted heterocycloalkylene, substituted arylene, and substituted
11 heteroarylene are substituted only with at least one substituent
12 independently selected from the group consisting of -OH, unsubstituted
13 (C₁-C₃)alkyl, unsubstituted 2 to 5 membered heteroalkyl, unsubstituted
14 (C₅-C₇) membered cycloalkyl, substituted 5 to 7 membered
15 heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl.

1 5. A method in accordance with claim 3 in which
2 each substituted alkyl, substituted heteroalkyl, substituted cycloalkyl, substituted
3 heterocycloalkyl, substituted aryl, and substituted heteroaryl are
4 substituted only with at least one substituent independently selected from
5 the group consisting of -OH, unsubstituted (C₁-C₃)alkyl, unsubstituted (C₅-
6 C₇) membered cycloalkyl, and unsubstituted phenyl; and
7 said substituted alkylene, substituted heteroalkylene, substituted cycloalkylene,
8 substituted heterocycloalkylene, substituted arylene, and substituted
9 heteroarylene are substituted only with at least one substituent
10 independently selected from the group consisting of -OH, unsubstituted
11 (C₁-C₃)alkyl, unsubstituted (C₅-C₇) membered cycloalkyl, and
12 unsubstituted phenyl.

1 6. A method in accordance with claim 3 in which
2 each substituted alkyl, substituted heteroalkyl, substituted cycloalkyl, substituted
3 heterocycloalkyl, substituted aryl, and substituted heteroaryl are
4 substituted only with at least one unsubstituted (C₁-C₃)alkyl; and
5 said substituted alkylene, substituted heteroalkylene, substituted cycloalkylene,
6 substituted heterocycloalkylene, substituted arylene, and substituted
7 heteroarylene are substituted only with at least one (C₁-C₃)alkyl.

1 7. A method in accordance with claim 3 in which
2 A is a member independently selected from the group consisting of -OR⁴,
3 unsubstituted (C₁-C₁₀)alkyl, unsubstituted 2 to 12 membered heteroalkyl,

4 unsubstituted (C₃-C₇)cycloalkyl, unsubstituted 5 to 7 membered
5 heterocycloalkyl, unsubstituted aryl, and unsubstituted heteroaryl,
6 wherein R⁴ is a member selected from the group consisting of hydrogen,
7 unsubstituted (C₁-C₁₀)alkyl, unsubstituted 2 to 12 membered
8 heteroalkyl, unsubstituted (C₃-C₇)cycloalkyl, unsubstituted 5 to 7
9 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted
10 heteroaryl;

11 R is a member selected from the group consisting of unsubstituted (C₁-
12 C₁₀)alkylene, unsubstituted 2 to 10 membered heteroalkylene,
13 unsubstituted (C₃-C₇)cycloalkylene, unsubstituted 5 to 7 membered
14 heterocycloalkylene, unsubstituted arylene, and unsubstituted
15 heteroarylene;

16 R¹, R², and R³ are members independently selected from the group consisting of
17 hydrogen, unsubstituted (C₁-C₂₀)alkyl, hydroxy-substituted (C₁-C₂₀)alkyl,
18 amine-substituted (C₁-C₂₀)alkyl, unsubstituted 2 to 20 membered
19 heteroalkyl, unsubstituted (C₃-C₇)cycloalkyl, unsubstituted 5 to 7
20 membered heterocycloalkyl, unsubstituted aryl, and unsubstituted
21 heteroaryl.

1 8. A method in accordance with claim 3
2 A is a member independently selected from the group consisting of -OR⁴,
3 unsubstituted (C₁-C₁₀)alkyl, unsubstituted 3 to 12 membered alkylether,
4 unsubstituted (C₃-C₇)cycloalkyl, and unsubstituted phenyl,
5 wherein R⁴ is a member selected from the group consisting of hydrogen,
6 unsubstituted (C₁-C₁₀)alkyl, unsubstituted 3 to 12 membered
7 alkylether, unsubstituted (C₃-C₇)cycloalkyl, and unsubstituted
8 phenyl;

9 R is unsubstituted (C₁-C₁₀)alkylene;
10 R¹, R², and R³ are members independently selected from the group consisting of
11 hydrogen, unsubstituted (C₁-C₂₀)alkyl, unsubstituted alkylether, hydroxy-
12 substituted (C₁-C₂₀)alkyl, amine-substituted (C₁-C₂₀)alkyl, unsubstituted
13 (C₃-C₇)cycloalkyl, and unsubstituted phenyl.

1 9. A method in accordance with claim 3 in which

A is a member independently selected from the group consisting of -OR⁴, unsubstituted (C₁-C₄)alkyl, unsubstituted 3 to 8 membered alkylether, unsubstituted (C₅-C₇)cycloalkyl, and unsubstituted phenyl, wherein R⁴ is a member selected from the group consisting of hydrogen, unsubstituted (C₁-C₈)alkyl, unsubstituted 3 to 8 membered alkylether, unsubstituted (C₅-C₇)cycloalkyl, and unsubstituted phenyl;

R is unsubstituted (C₁-C₁₀)alkylene;

R¹, R², and R³ are members independently selected from the group consisting of hydrogen, unsubstituted (C₁-C₂₀)alkyl, unsubstituted alkylether, hydroxy-substituted (C₁-C₂₀)alkyl, amine-substituted (C₁-C₂₀)alkyl, unsubstituted (C₅-C₇)cycloalkyl, and unsubstituted phenyl.

10. A method in accordance with claim 3 in which

A is a member independently selected from the group consisting of -OR⁴, unsubstituted (C₁-C₄)alkyl, and unsubstituted 3 to 8 membered alkylether, wherein R⁴ is a member selected from the group consisting of hydrogen, unsubstituted (C₁-C₈)alkyl, and unsubstituted 3 to 8 membered alkylether,

R is unsubstituted (C₁-C₁₀)alkylene;

R¹, R², and R³ are members independently selected from the group consisting of hydrogen, unsubstituted (C₁-C₂₀)alkyl, unsubstituted alkylether, hydroxy-substituted (C₁-C₂₀)alkyl, and amine-substituted (C₁-C₂₀)alkyl.

11. A method in accordance with claim 10 in which R¹, R², and R³ are members independently selected from the group consisting of -(CH₂)_qOCH₃, -(CH₂)_qOH, -(CH₂)_qO(CH₂)_tCH₃, -(CH₂)_qNHCH₃, -(CH₂)_qNH₂, -(CH₂)_qN(CH₃)₂ and -(CH₂)_qNH₂(CH₂)_tCH₃, wherein q and t are integers independently selected from 0 to 10.

12. A method in accordance with claim 10 in which R¹, R², and R³ are members independently selected from the group consisting of -CH₂CH₂OCH₃ and -CH₂CH₂OCH₂CH₂CH₃.

1 13. A method in accordance with claim 10 in which R¹, R², and R³ are
2 members independently selected from the group consisting of -CH₂CH₂OH and
3 -CH₂CH₂CH₂CH(OH)CH₃.

1 14. A method in accordance with claim 10 in which R¹, R², and R³ are
2 members independently selected from the group consisting of -CH₂CH₂NH₂ and
3 -CH₂CH₂N(CH₃)₂.

1 15. A method in accordance with claim 10 in which R¹, R², and R³ are
2 members independently selected from the group consisting of methyl, octadecyl, didecyl,
3 and tetradecyl.

1 16. A method in accordance with claim 2 in which said quaternary
2 ammonium organosilane reagent is 3-(trimethoxysilyl)propyldimethyloctadecyl
3 ammonium chloride.

1 17. A method in accordance with claim 2 in which said quaternary
2 ammonium organosilane reagent is 3-(trimethoxysilyl)propyldidecylmethyl ammonium
3 chloride.

1 18. A method in accordance with claim 2 in which said quaternary
2 ammonium organosilane reagent is 3-(trimethoxysilyl)propyldimethyltetradecyl
3 ammonium chloride.

1 19. A method in accordance with claim 1 in which said liquid is
2 contacted with at least one additional solid phase carrier coated with a different
3 quaternary ammonium organosilane coating.

1 20. A method in accordance with claim 1 in which said
2 microorganisms are member selected from the group consisting of gram-positive and
3 gram-negative bacteria.

1 21. A method in accordance with claim 1 in which said
2 microorganisms are viruses.

1 22. A method in accordance with claim 1 in which said
2 microorganisms are fungi.

1 23. A method in accordance with claim 1 in which said
2 microorganisms are a member selected from the group consisting of algae and mold.

1 24. A method in accordance with claim 1 in which said
2 microorganisms are yeast.

1 25. A method in accordance with claim 1 in which said
2 microorganisms are spores.

1 26. A method in accordance with claim 1 in which said liquid is a
2 member selected from the group consisting of water and aqueous solution.

1 27. A method in accordance with claim 26 in which said solid phase
2 carrier comprises a material selected from the group consisting of glass, silica, sand,
3 quartz, flint, zeolite, anthracite, activated carbon, garnet, ilmenite, beryl, non-hydrous
4 aluminum silicate, oxides of iron and titanium, diatomaceous earth, pozzolan, metal,
5 ceramic, and organic plastic.

1 28. A method in accordance with claim 1 in which said liquid is
2 contacted with an additional solid phase carrier, wherein said additional solid phase
3 carrier comprises a different material than said solid phase carrier.

PATENT

Attorney Docket No.: 020511-000310US

**ANTIMICROBIAL QUATERNARY AMMONIUM ORGANOSILANE
COATINGS****ABSTRACT OF THE DISCLOSURE**

The present invention provides novel solid phase carriers coated with a quaternary ammonium organosilane coating for use in reducing or eliminating the viable number of microorganisms in a liquid. The invention is useful in a wide variety applications, such as water purification and reduction of harmful microorganisms in liquid foodstuffs.

60219400 v1

Attorney Docket No.: 020511-000310US
Client Ref. No.:

PTO/BB/01A (08-03)

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention | **ANTIMICROBIAL QUATERNARY AMMONIUM ORGANOSILANE COATINGS.**

As the below named inventor(s), I/we declare that:

This declaration is directed to:

- ☒ The attached application, or
- ☐ Application No. _____, filed on May 19, 2004,
- ☐ as amended on _____ (if applicable);

I/we believe that I/we am/are the original and first inventor(s) of the subject matter which is claimed and for which a patent is sought;

I/we have reviewed and understand the contents of the above-identified application, including the claims, as amended by any amendment specifically referred to above;

I/we acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me/us to be material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT International filing date of the continuation-in-part application.

All statements made herein of my/our own knowledge are true, all statements made herein on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001, and may jeopardize the validity of the application or any patent issuing thereon.

FULL NAME OF INVENTOR(S)

Inventor 1 William Peterson Date: _____
Signature: _____ Citizen of: United States

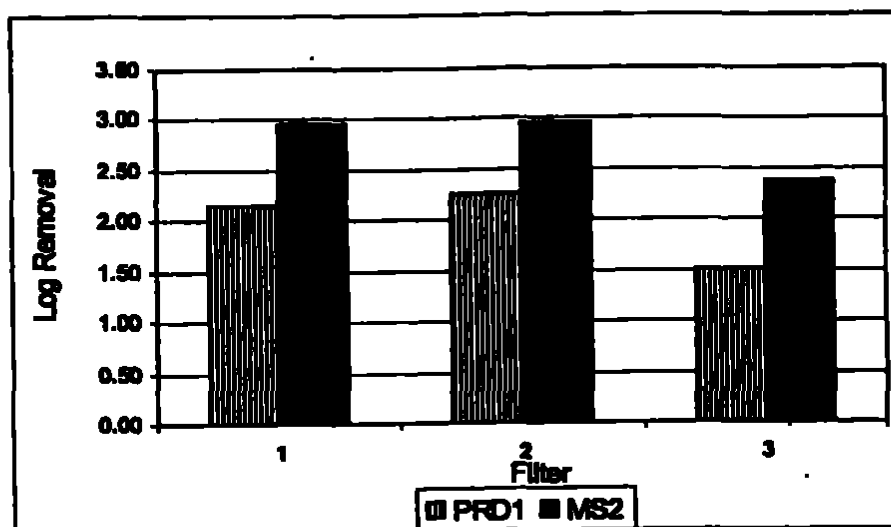
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Inventor 4 _____ Date: _____
Signature: _____ Citizen of: _____

☐ Additional inventors are being named on additional form(s) attached hereto.

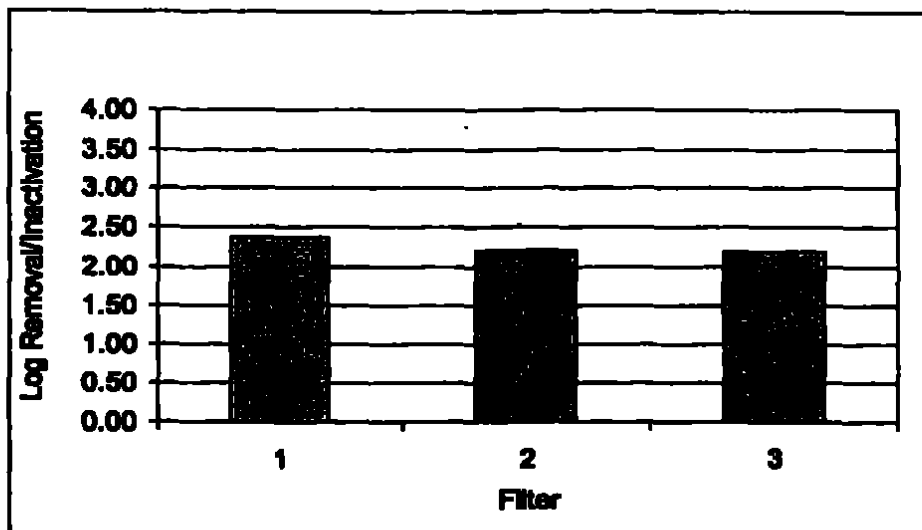
FIG. 1



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FIG. 2

A



B

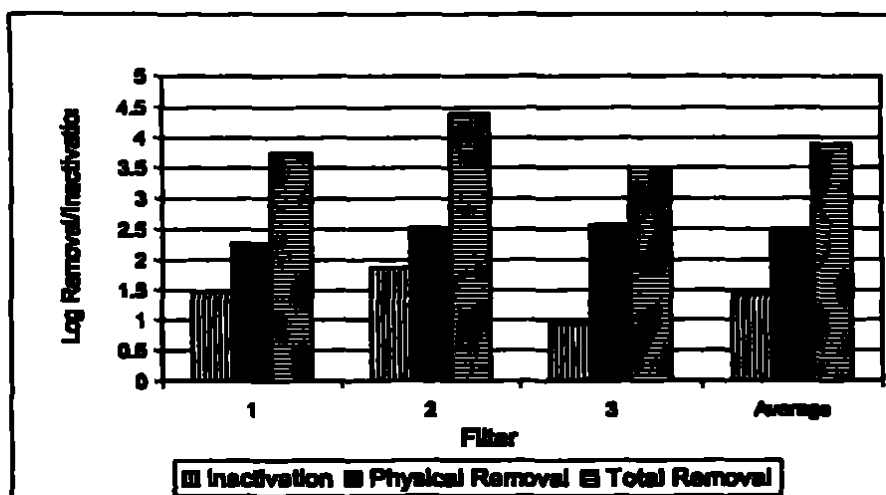


FIG. 3

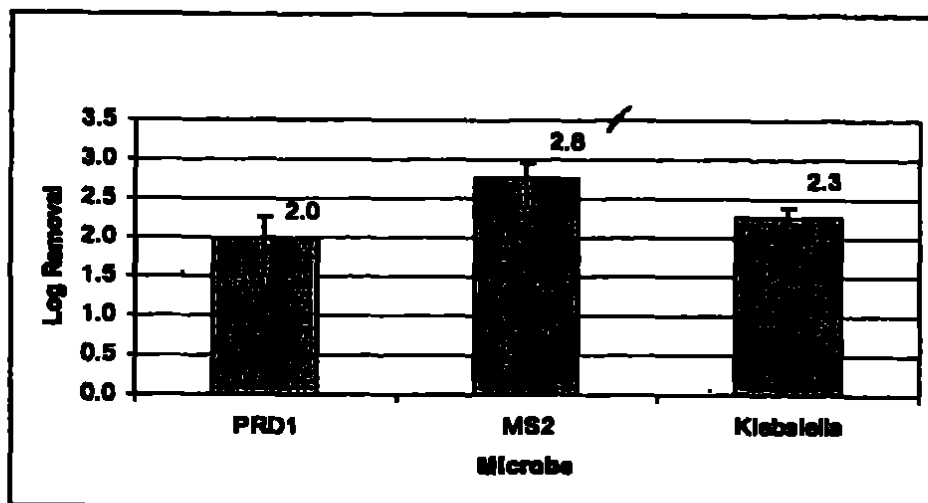
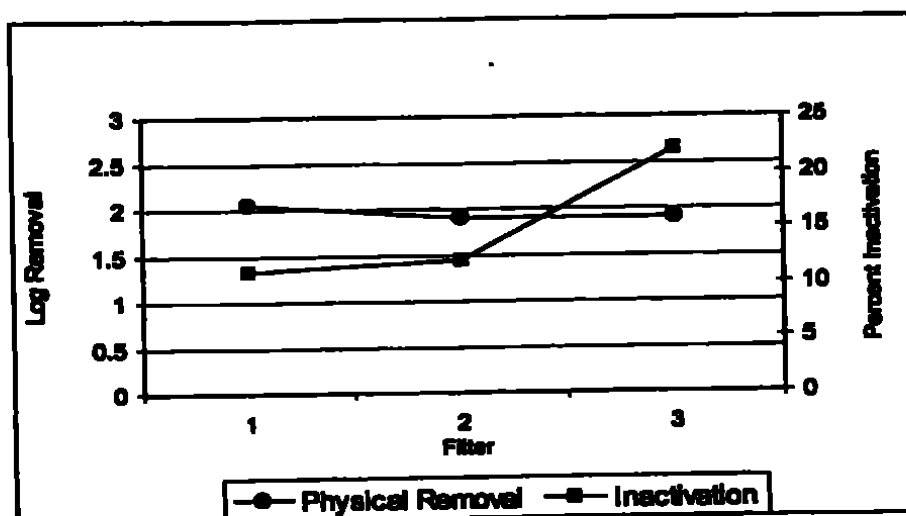


FIG. 4



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FIG. 5

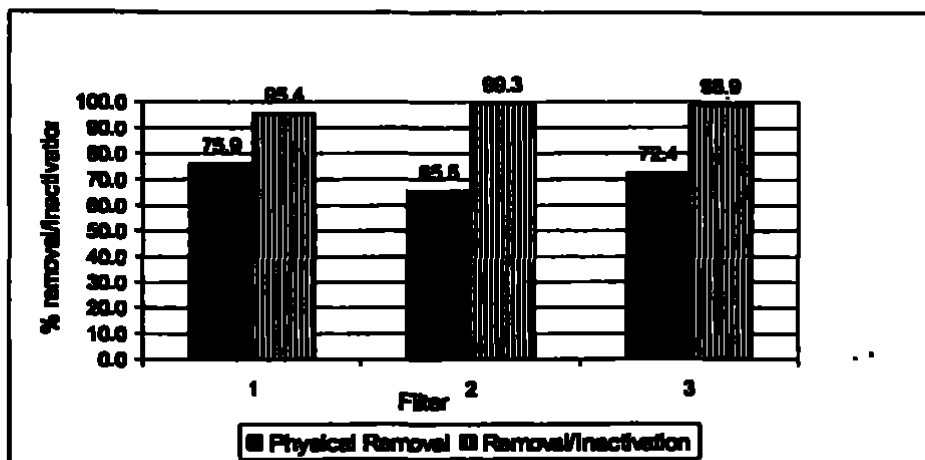
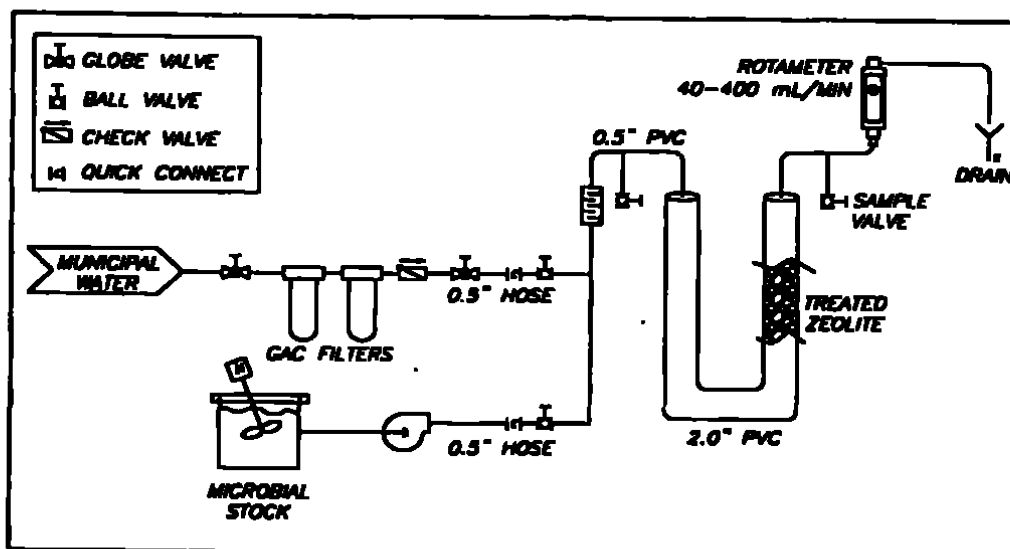


FIG. 6



Application Data Sheet**Application Information****Application number::****Filing Date::** 05/19/04**Application Type::** Regular**Subject Matter::** Utility**Suggested classification::****Suggested Group Art Unit::****CD-ROM or CD-R??::****Number of CD disks::****Number of copies of CDs::****Sequence Submission::****Computer Readable Form (CRF)?::****Number of copies of CRF::****Title::** ANTIMICROBIAL QUATERNARY AMMONIUM
ORGANOSILANE COATINGS**Attorney Docket Number::** 020511-000310US**Request for Early Publication::** No**Request for Non-Publication::** No**Suggested Drawing Figure::****Total Drawing Sheets::** 6**Small Entity?::** Yes**Latin name::****Variety denomination name::****Petition included?::** No**Petition Type::****Licensed US Govt. Agency::****Contract or Grant Numbers One::****Secrecy Order in Parent Appl.::** No

117
17

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Correspondence Customer Number:: 20350

Representative Information

Representative Customer Number:: 20350

Domestic Priority Information

Application::	Continuity Type::	Parent Application::	Parent Filing Date::
This Application	An Appn claiming benefit under 35 USC 119(e) of	60/472,429	May 22, 1003

Foreign Priority Information

Country::	Application number::	Filing Date::
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Assignee Information

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Country of mailing address::

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Date Mailed: 10/04/2004

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Applicant(s)

William Peterson, Phoenix, AZ;
 Renee E. Berman, Chandler, AZ;

Assignment For Published Patent Application

COATING SYSTEMS LABORATORIES, INC.

Power of Attorney: None**Domestic Priority data as claimed by applicant**

This appln claims benefit of 60/472,429 05/22/2003

Foreign Applications

If Required, Foreign Filing License Granted: 07/19/2004

The number of your priority application, to be used for filing abroad under the Paris Convention is,
US10/850,121

Projected Publication Date: 01/13/2005

Non-Publication Request: No

JL

PETITORIO



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FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

1

SOLICITUD DE:

☒

Patente de Invención

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Patente de Modelo de Utilidad

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Capítulo I

☒

Capítulo II

2

SOLICITANTE
(71)Nombre: COATING SYSTEMS
LABORATORIES, INC. y NORTHERN
GRAVEL COMPANYDirección: 221 East Chilton Drive y
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Muscatine, Iowa
(E.U.A.)

Lugar de Constitución:

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C.C. ☐ NIT ☐C.E. ☐ Otro ☐

Cual

Número

3

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C.C. ☒ NIT ☐C.E. ☐ OTRO ☐

Cual

Número 79.397.879 de TP 68.985 del
Bogotá C.S.J.

4

INVENTOR(ES)
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5

PCT (88)

Solicitud Internacional No. PCT/US2004/15853Fecha: 19/05/04Publicación Internacional No. WO 2004/105687 A3Fecha: 09/12/04

6

Título (64) RECUBRIMIENTOS ANTIMICROBIANOS DE ORGANOSILANO AMONIO CUATERNARIO

7

Clasificación Internacional (51) A51K 9/14

8

Prioridad

Si

☒

No

☐

(33) País de origen

E.U.A.

(32) Fecha

22.05.2003

(31) Número de Solicitud

60/472,429

9

Comprobante de pago N°:

Fecha:

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

122
83

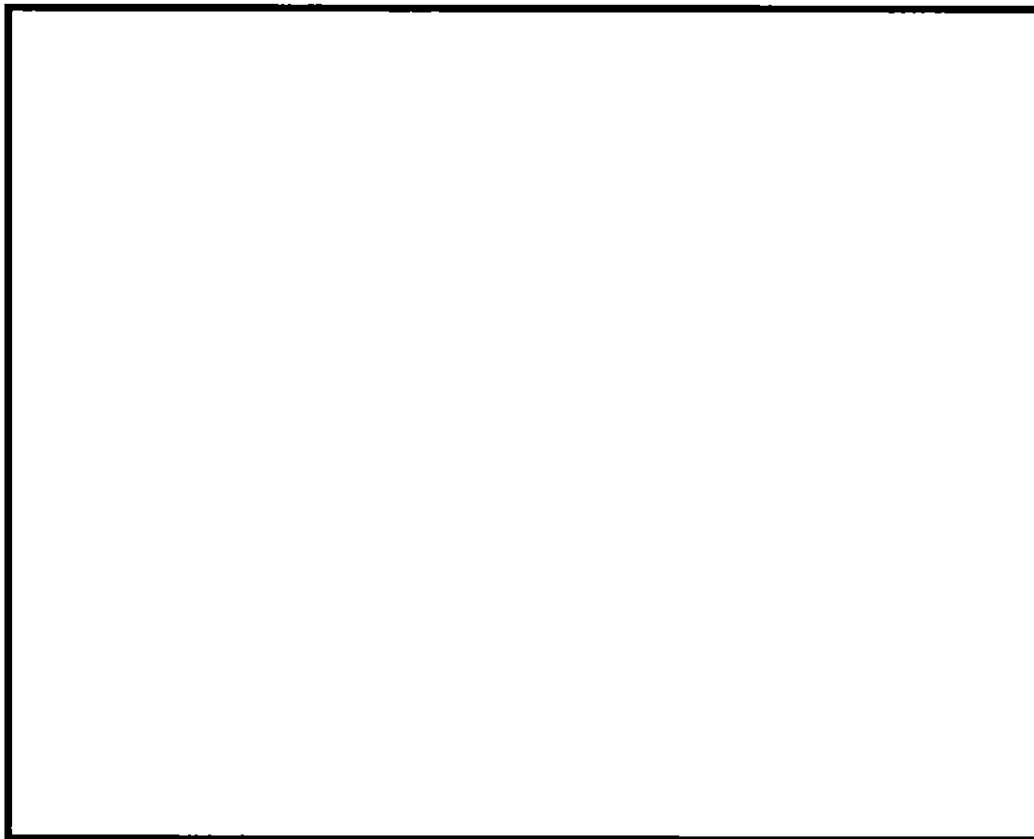
10

ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso
- ☐ Certificado de existencia y representación legal cuando el solicitante sea persona jurídica
- ☐ Documento de Cesión del Inventor al solicitante o a su acusante
- ☐ Declaraciones
- ☐ Copia de la solicitud Internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ 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 de material biológico.
- ☐ Arte final 12 x 12
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ Otros

11

FIGURA CARACTERISTICA



12

Solicito la concesión de patente,

NOMBRE: LUIS FELIPE CASTILLO GIBSON

FIRMA:

C.C. 78'397.879
de Bogotá

T.P. 88,995
del C.S.J.

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