



Industria y Comercio

SUPERINTENDENCIA

Delegatura de propiedad Industrial

División de Nuevas Creaciones

PCT
SOLICITUD

PATENTE DE INVENCION

21 EXPEDIENTE No

05 123300

54 TÍTULO Composiciones y Métodos para oscure-
cer e impartir propiedades de resistencia al
corrosión al zinc u otros metales activos

51 CLASIFICACIÓN INTERNACIONAL

71 SOLICITANTE Metal Coatings International Inc

DOMICILIO Ohio, Estados Unidos

74 APODERADO Dilra Rodriguez D'Aleman

22 BOGOTÁ, D C , Dic 5/05

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

1) SOLICITUD DE:			
☒ Patente de invención		☐ Patente de Modelo de Utilidad	
☐ Capítulo I.		☒ Capítulo II.	
2) S LICITANTE (71)	Nombre: METAL COATINGS INTERNATIONAL INC.		IDENTIFICACIÓN C.C. ☐ NIT: ☐ C.E. ☐ OTRO ☐ Cual _____ NÚMERO _____
	Dirección: 275 Industrial Parkway Chardon, Ohio 44024-1083, Estados Unidos Nacionalidad o domicilio: Ohio, Estados Unidos Lugar de constitución: Delaware, Estados Unidos		
	Teléfono: E. Mail:	Fax:	
3) REPRESENTANTE APODERADO	Nombre: DILIA MARÍA RODRÍGUEZ D'ALEMAN		IDENTIFICACIÓN C.C. ☒ NIT: ☐ C.E. ☐ OTRO ☐ NÚMERO: 41.854.882 TP: 20824 CSJ
	Dirección: Carrera 11 N°. 86-53 Piso 6 Bogotá D.C. Teléfono: 6181088 Fax: 6350824 E. Mail: info@clarkemodet.com.co		
4) INVENTOR (ES) (72)	Nombre: 1. Michelle R. PEARCE. 2. Brian G. STRAKA. 3. Donald J. GUHDE. 4. Terry E. DORSETT Dirección: 1. 9810 Kile Road, Chardon Ohio 44024 , Estados Unidos. 2. 1569 Trotter Lane Palmsville, Ohio 44077. Estados Unidos. 3. 160 East 191 Street Euclid, Ohio 44119. Estados Unidos. 4. 11205 Hosford Road Chardon, Ohio 44024. Estados Unidos. Nacionalidad o Domicilio: 1. Estados Unidos. 2. Estados Unidos. 3 Estados Unidos. 4. Estados Unidos.		
5) PCT (86) Solicitud Internacional No.PCT/US2004/017786 Fecha: Junio 4, 2004 Publicación Internacional No. WO 2004/108407 Fecha: Diciembre 16, 2004			
6) Título (54) COMPOSICIONES PARA OSCURECER E IMPARTIR PROPIEDADES DE RESISTENCIA A LA CORROSION AL ZINC U OTROS METALES ACTIVOS.			
7) Clasificación Internacional: B32B 15/04			
8) PRIORIDAD		33) País de Origen	(32) Fecha
SI ☒ NO ☐		Estados Unidos	Junio 5, 2003
			(31) Número de Solicitud 60/476.119
9) Comprobante de pago N°. 05.79.894 Fecha:Octubre 14 , 2005 Comprobante de pag N°. 05.91.289 Fecha: N viembre 29 , 2005 C mprobante de pag N°. 05.90.614 Fecha:Noviembre 25 , 2005			
Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina			

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Z

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 79,894
FECHA : OCTUBRE 14 DE 2005

SUPERINDUSTRIA Y COMERCIO
Radicacion : 05123300 00000000 Folios: 226
Fecha (AMD): 2005-12-05 16:56:25
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	45331664	13/10/2005	5,064,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		85 EXAMEN DE PATENTABILIDAD DE INVEN	371,000.00
		TOTAL :	\$ 371,000.00

SON: TRESCIENTOS SETENTA Y UNO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

119
3

SUPERINDUSTRIA Y COMERCIO
Radicacion : 05123300 00000000 Folios: 226
Fecha (AMD): 2005-12-05 16:56:25
Tramite : 011 PCI-PATENT 379 FASE HACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 91,289
FECHA : NOVIEMBRE 29 DE 2005

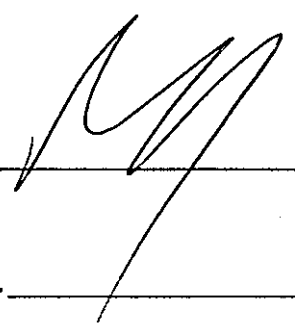
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	42212697	29/11/2005	6,780,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-08	PRORROGA DE TERMINOS	66,000.00
		TOTAL :	\$ 66,000.00

SON: SESENTA Y SEIS MIL PESOS

RESPONSABLE : 
RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 90,614
FECHA : NOVIEMBRE 25 DE 2005

SUPERINDUSTRIA Y COMERCIO
Radicacion : 05123300 00000000 Folios: 226
Fecha (AMD): 2005-12-05 16:56:25
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	42212701	25/11/2005	4,397,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	21 CERTIFICACIONES
			10,000.00
		TOTAL :	\$ 10,000.00

SON: DIEZ MIL PESOS

RESPONSABLE : _____

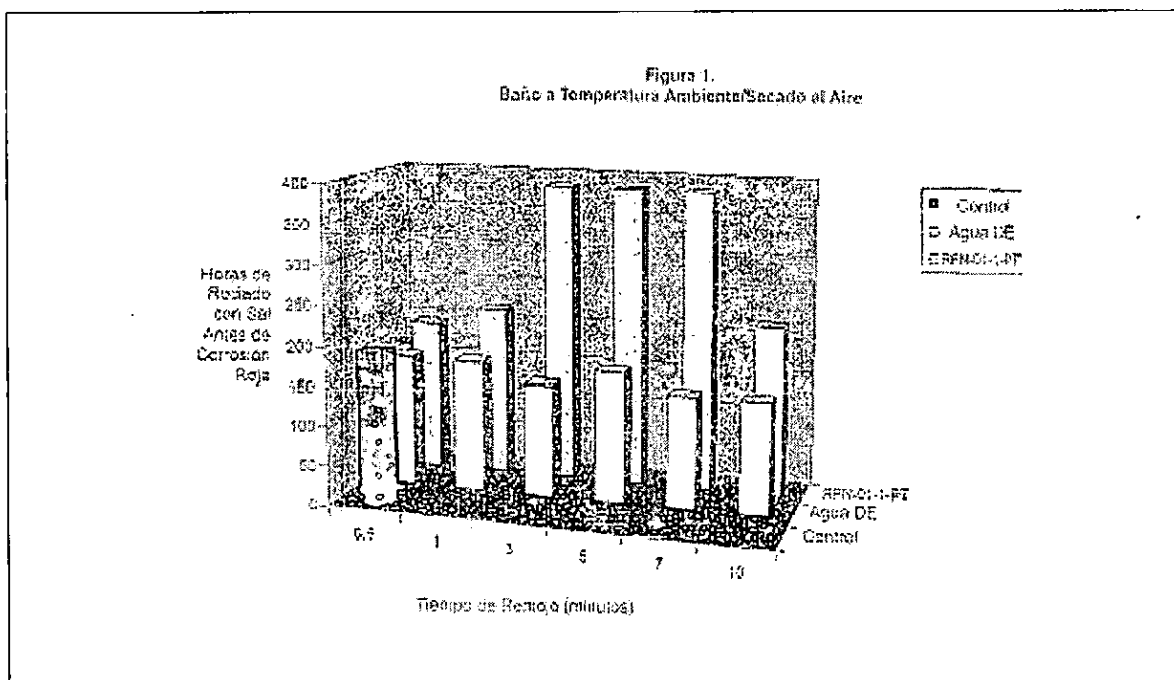
RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

10)

ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Comprobante de pago por reivindicación de prioridad
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona Jurídica
- ☒ Poderes, si fuera el caso
- ☐ Documento de cesión del inventor al solicitante o a su causante
- ☐ Declaraciones
- ☒ Copia de la solicitud Internacional. (Resumen, descripción, reivindicación, Dibujos).
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicación, Dibujos)
- ☒ Copia del examen preliminar efectuado por la IPEA
- ☐ De ser el caso, copia del contrato de acceso
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas
- ☐ De ser el caso, certificado de depósito del material biológico
- ☐ Arte final 12 x 12 y 6 x 6 cm
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionados parcial o totalmente con la invención de esta solicitud.
- ☒ Otros:
 1. Reporte búsqueda internacional
 2. Opinión escrita
 3. Solicitud PCT

11) FIGURA CARACTERÍSTICA:



12) Solicitud concesión de la patente,

NOMBRE: DILIA RODRÍGUEZ D'ALEMAN

FIRMA:

C.C. 41.654.882 de Bogotá TP 20824 CSJ

Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina

PODER

Yo (nosotros), abajo firmante(s)

George C. Palek

en mi (nuestro) carácter de representante(s) legales de

METAL COATINGS INTERNATIONAL INC.

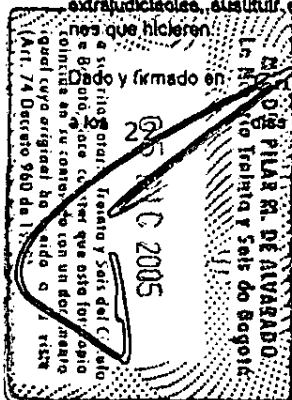
una sociedad organizada y existente de acuerdo con las leyes de

Delaware, EEUU

y en actual cumplimiento de su objeto social, con domicilio en
275 Industrial Parkway, Chardon,
Ohio, Estados Unidos

por el presente instrumento confiero (conferimos) poder especial a favor de DILIA MARIA RODRIGUEZ D'ALEMAN, tp. 20824 y CLAUDIA LUCIA CARO RAMIREZ, tp. 36448, con domicilio en Santa Fé de Bogotá, Colombia, para que actuando en su orden en nombre del (de la) otorgante le (la) representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden Administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro en lo referente a los siguientes asuntos:

- 1) Solicitar, tramitar, obtener y/o registrar cualquiera de las modalidades de Propiedad Industrial, tales como: patentes de invención, modelos de utilidad; diseños industriales, variedades vegetales; marcas, lemas, nombres y enseñas comerciales y denominaciones de origen; así como sus renovaciones, prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias
- 2) Solicitar, tramitar, obtener y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how.
- 3) Solicitar, tramitar, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento; así como sus renovaciones o prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.
- 4) Ejercer acciones de oposición, observación, reclamos, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados con derechos derivados de los asuntos arriba indicados y en contra de la competencia desleal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrá(n) intervenir en juicios civiles, comerciales, penales, contencioso-administrativos, tutelas y de policía, en acciones o juicios promovidos por el (la) mandante o en contra el (ella).
- 5) En el ejercicio de este mandato los mandatarios arriba mencionados quedan facultados para: conciliar, cancelar, transigir, comprometer en árbitros, desistír, recibir y tomar posesión de la cosa objeto de litigio y renunciar o desistír a derechos concedidos o en curso de concesión, admitir los hechos del proceso.
- 6) Ratificar o no la agencia oficiosa.
- 7) Así mismo faculto (facultamos) a los mencionados apoderados para recibir notificaciones y designar apoderados judiciales o extrajudiciales, sustituir el presente poder y revocar las sustituciones que hicieren.



Dado y firmado en Chardon, Ohio, Estados Unidos el 22 de julio de 1997 on this 22nd day of July of 1997

George C. Palek
Firma / signature

George C. Palek, Treasurer and C.O.O.

POWER OF ATTORNEY

I (We), the undersigned

George C. Palek

legal representative(s) of

Metal Coatings International Inc.

an organization existing under the laws of

Delaware, U.S.A.

and in present execution of its business activity, domiciled at

275 Industrial Parkway, Chardon, Ohio,

do hereby grant POWER OF ATTORNEY to DILIA MARIA RODRIGUEZ D'ALEMAN, tp. 20824 and CLAUDIA LUCIA CARO RAMIREZ, tp. 36448, residing in Santa Fé de Bogotá, Colombia, to act in the order of their appointment in behalf of grantor before any entity, authority and/or natural or juridical person, specially before those Administrative, Administrative-Contentious, Judicial, arbitration courts, and/or any other, in all matters concerning the following:

- 1) To apply, process, obtain and/or register any of the modalities of Industrial Property, such as: Patents of Invention, Utility Models; Designs, vegetal varieties; Marks, Slogans, Trade Names and emblems and appellations of Origin, as well as their renewals, extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 2) To apply, process, obtain and/or register copyrights of any kind as well as protection of industrial secrets or know-how.
- 3) To apply, process, obtain and/or register sanitary registrations, operating authorizations and/or licenses; as well as their renewals or extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 4) To bring actions of opposition, observations, claims, reconsideration, appeal or legal remedies, cancellations, nullity, protection to the consumer, granting of licenses, protection of trade secrets and other actions related with rights derived from the above-mentioned matters and against the unfair competition, actions resulting from the obtention or exploitation of licenses, recovering damages actions. They can also intervene or participate in Civil, Commercial, Criminal or Contentious-Administrative Trials; the actions for writ mandamus, police actions; in actions, lawsuits or litigations instituted by the grantor or against him.
- 5) To the effect of this mandate the above-named proxy are empowered to: conciliate, cancel, settle, submit to arbitration, withdraw and to receive and take possession of the litigation related object and waive or renounce the rights granted or in process of granting, admit the facts of the case.
- 6) To ratify or not the officious agency.
- 7) I (we) hereby appoint the afore mentioned attorneys with powers to receive notifications and to designate judicial and extrajudicial attorneys, substitute this Power of Attorney and to revoke such substitutions.



Recpto: *[Signature]*
00740017334700
J. P. 23. 448 11/10/97
FROM: CLORKE M BRASILE

[Signature]
C.C. 448 11/10/97
PHONE NO. : 438 11/10/97
P.O. Box 281997 May 28 1997

CERTIFICADO NOTARIAL (SOCIEDADES)

(Poderes otorgados en: El Salvador, Estados Unidos, Mexico y Venezuela)

A los _____ días del mes de _____ de _____ el Notario que suscribe DA FE de que

(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____

_____ firmó de su puño y letra el documento que antecede

2. Conoce al (a) otorgante y que este (a) está legalmente capacitado para el otorgamiento

3. El otorgante ha firmado el referido documento en su

carácter de _____

de la persona jurídica _____

4. La citada persona jurídica con sede en _____

está legalmente constituida, que tiene actualmente existencia legal y que el acto para el cual se ha otorgado este poder está comprendido entre los que constituyen su objeto social.

5. El otorgante tiene efectivamente la representación que ostenta, que esta es legítima y que está facultado para otorgar este poder.

6. Las anteriores certificaciones de los puntos 3, 4 y 5, me constan porque he tenido a la vista los siguientes documentos auténticos:

Notario Público

NOTA: A continuación de lo anterior, el Consul de Colombia debe autenticar la firma del Notario Público.

CERTIFICADO NOTARIAL (INDIVIDUOS)

A los _____ días del mes de _____ de _____ el Notario que suscribe DA FE de que:

(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____

_____ firmó en su presencia el documento que antecede, conoce al otorgante y que este está legalmente capacitado para el otorgamiento.

Notario Público

NOTA: A continuación de lo anterior, el Consul de Colombia debe autenticar la firma del Notario Público.

Para todos los demás países el Señor Consul de Colombia o ante quien se otorgue, debe expedir una certificación dejando constancia: 1) de la existencia legal de la sociedad, 2) de que esta ejerce actualmente su objeto social, y 3) de que la persona o personas que otorgan el poder están facultadas para hacerlo, dejando constancia así mismo de que tuvo a la vista las pruebas que acreditan tales circunstancias.

NOTARIAL CERTIFICATE (CORPORATIONS)

(Powers of attorney granted in: El Salvador, Mexico, U.S.A. and Venezuela)

This 12th day of May, 1998, the undersigned Notary CERTIFIES that

1. George C. Palek

(name of the person who signs the power of attorney)

of legal age and domiciled in _____

Mentor, Ohio, USA set his hand on the foregoing document

2. The grantor is to him personally known and that he/she has legal capacity to execute the document

3. The grantor has executed the foregoing document in

his capacity of President and CEO

of the juridical person _____

Metal Coatings International Inc.

4. The mentioned juridical person with place of business

in Chardon, Ohio, USA

is duly organized, has actual legal existence and that the purposes for which the power of attorney is granted are within the scope of its corporate purposes.

5. The grantor has in fact the referred quality and that his/her representation is legal and that he/she is empowered to grant this power of attorney.

6. I have based the above certifications 3, 4 and 5, on the following authentic documents which for such purpose were exhibited to me:

Minutes of Board of Directors Meetings

BRENDA L. HAVEL

Notary Public, State of Ohio

My Commission Expires August 7, 2001

Recorded in Ashtabula County

Brenda L. Havel

Notary Public

NOTA: Then the Colombian Consul must legalize the signature of the Notary Public.

NOTARIAL CERTIFICATE (INDIVIDUALS)

On this _____ day of _____ the undersigned Notary CERTIFIES that:

1. _____ (name of the person who signs the Power of Attorney)

of legal age and domiciled at _____

_____ signed in his presence the foregoing document, the grantor is to him personally known and that he/she has legal capacity to execute the document.

Notary Public

NOTA: Then the Colombian Consul must legalize the signature of the Notary Public.

For all other countries the Colombian Consul or before whom it is granted must issue a certification stating 1) the legal existence of the corporation, 2) that the corporate purposes are actually being accomplished, 3) that the person or persons who grant this Power of Attorney are empowered to do it. The Consul will certify also that the documents evidencing these circumstances were exhibited to him.



NO. 002106

I, Carol A. Mead, Clerk of the Court of Common Pleas, a court of Law and Record in said County, do hereby certify that BRENDA L. HAVEL before whom the proof or acknowledgement of the foregoing instrument was taken and whose signature appears to the foregoing certificate of proof or acknowledgement was at the date of said proof or acknowledgement, a NOTARY PUBLIC, in and for the State, duly authorized to take the same and certify affidavits and oaths, and to take and certify the proof and acknowledgement of deeds recorded in said State; and that I am well acquainted with his/her handwriting and verily believe that the signature to said certificate purporting to be his/hers is genuine.

THE STATE OF OHIO
Ashtabula County, ss

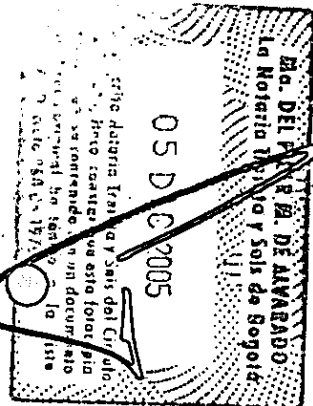
In Testimony Whereof, I have hereunto set my hand and affixed the seal of said Court at Jefferson, Ohio this 15th day of MAY 19 98

Carol A. Mead

Clerk

Carol J. Klingerman

Deputy Clerk





Consulado General de Colombia

500 NORTH MICHIGAN AVENUE, SUITE 2040
CHICAGO, ILLINOIS 60611

TEL. (312) 923-1196 FAX (312) 923-1197

No. 3913

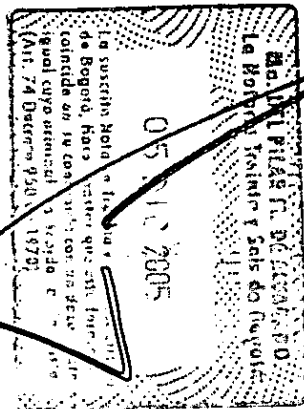
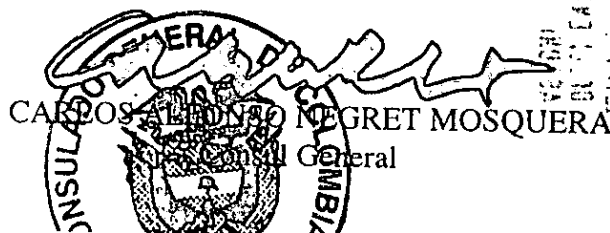
Chicago,

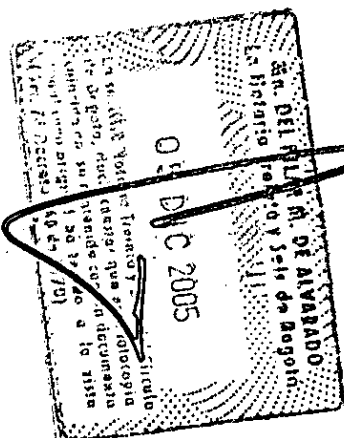
AUG 06 1991

El suscrito Cónsul General de Colombia, CERTIFICA que el señor Carretero, quien autoriza el presente documento, ejercía legalmente, en la fecha allí expresada, las funciones de Secretario de la Corte, y que la firma y sello que en el documento aparecen como suyos son los que usa y acostumbra en sus actos oficiales.

El Cónsul no asume responsabilidad alguna por el contenido del documento.

DERECHOS DE TIMBRE Y DERECHOS CONSULARES (VEINTIUN DOLARES US\$21.00).





MINISTERIO DE RELACIONES
EXTERIORES

219596

CUYA FIRMA APARECE EN
DOCUMENTO DESEMPER
LAS EDUCACIONES INDICADAS

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

97 SEP - 4 AM 9:47

JEFE DE LEGALIZACIONES
SANTAFE DE BOGOTA D.C.

[Handwritten signature]

Traducción Oficial No.97910 de un documento escrito en inglés, el cual para su identificación se sella con el sello del Traductor al mismo tiempo que la presente. Esta Traducción ha sido preparada por Ana María Salvetti, Traductora Oficial debidamente reconocida por el Ministerio de Relaciones Exteriores y aprobada por el Ministerio de Justicia mediante Resolución No.158 de 1991.

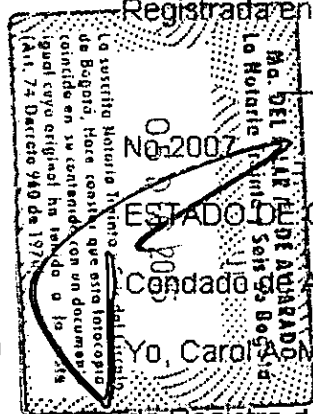
10 \$

(Se traducen sellos y legalizaciones que aparecen a continuación de un Poder escrito en inglés y español otorgado por la sociedad Metal Coatings International Inc. a favor de DILIA MARIA RODRIGUEZ D'ALEMAN y CLAUDIA LUCIA CARO RAMIREZ .)

Dado y firmado en Ohio, EE.UU., el 22 de julio de 1997 por (Firmado), ilegible, George C. Palek, Tesorero y P.F.O. Acepto, (Firmado), Claudia Lucía Caro, c.c. No.40.017.374 de Tunja, T.P.A. No.36.448 Minjusticia.

(al dorso, en inglés y español): CERTIFICADO NOTARIAL (Sociedades) referente a la existencia y representación de la sociedad mencionada. (Firmado), Brenda L. Havel, Notario Público. Sello en tinta: BRENDA L. HAVEL, Notario Público, Estado de Ohio. Mi comisión expira 7 de agosto del 2001.

Registrada en el Condado de Ashtabula. Sello circular en relieve.



Yo, Carol A. Mead, Escribano de la Corte de Causas Comunes, una corte Legal y de Registro de dicho Condado, por medio del presente certifico que Brenda L. Havel, ante quien la prueba o reconocimiento del instrumento que antecede fue tomado y cuya firma aparece en el anterior certificado de prueba o reconocimiento era en la fecha de dicha prueba o reconocimiento, un NOTARIO PUBLICO, en y para el Estado, debidamente autorizado para tomarlo y certificar declaraciones

juramentadas y juramentos, y para tomar y certificar la prueba y reconocimiento de escrituras registradas en dicho Estado; y que estoy bien familiarizado con su caligrafía y sinceramente creo que la firma en dicho certificado que pretende ser la suya, es auténtica.

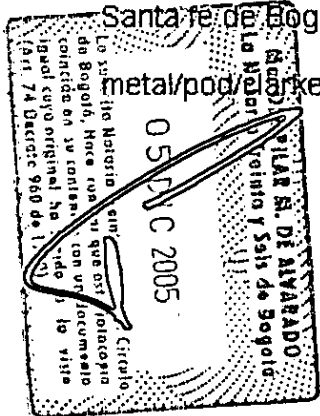
En testimonio de lo cual, he firmado y estampado el sello de dicha Corte en Jefferson, Ohio, hoy 31 de julio de 1997. (Firmado), Carol A. Mead., Escribano.
Sello circular en relieve.

(en español): Certificación No. **3913** del 6 de agosto de 1997 de la firma que antecede por el Consulado de Colombia en Chicago. Pagado impuesto de timbre y derechos consulares. (Firmado), Carlos Alfonso Negret Mosquera. Sello consular en tinta. Legalización No. **219596** del 4 de septiembre de 1997 de la firma que antecede por el Ministerio de Relaciones Exteriores. (Firmado), Jefe Legalizaciones.

Es Traducción fiel y completa tomada de su original en inglés a la cual me remito.

Santa Fe de Bogotá, 12 de septiembre de 1997

metal/pod/arte



Ana Maria Salvetti
ANA MARIA SALVETTI
TRADUCTORA OFICIAL
INGLES - ITALIANO - ESPAÑOL
RES. 153/91 MINJUSTICIA

12 4

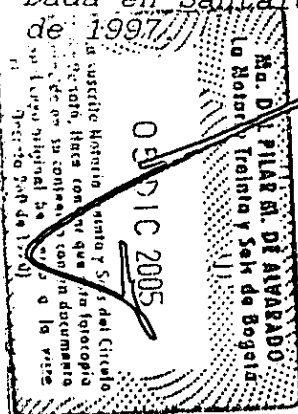
**EL SUSCRITO JEFE DEL AREA DE
LEGALIZACIONES DEL MINISTERIO DE
RELACIONES EXTERIORES**

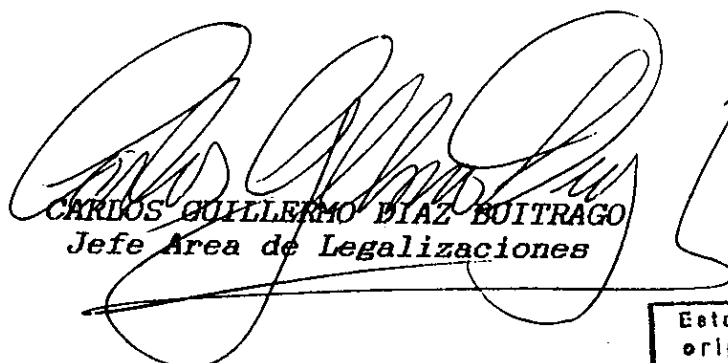
CERTIFICA

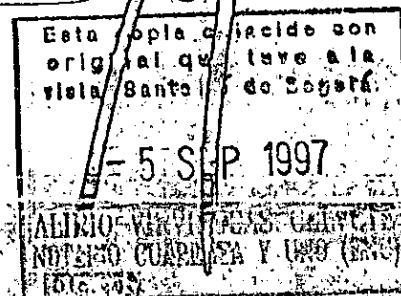
Que revisados los registros que se llevan en la oficina de Legalizaciones aparece la firma de la señora **ANA MARIA SALVETTI GOMEZ** como Traductora e Intérprete Oficial para los idiomas **INGLES-ESPAÑOL, ESPAÑOL-INGLES, ITALIANO-ESPAÑOL, ESPAÑOL-ITALIANO**, según resolución 158 del 11 de febrero de 1991.

La anterior certificación se expide a solicitud de la interesada quien se identificó con cédula de ciudadanía nro. 51.773.103 expedida en Bogotá.

Dada en Santafé de Bogotá, D.C., a los diez (10) días de julio de 1997.




CARLOS GUILLERMO DIAZ BOTTRAGO
Jefe Area de Legalizaciones



TRADUCCIÓN OFICIAL DEL CERTIFICADO NOTARIAL QUE ACOMPAÑA/
PODER QUE METAL COATINGS INTERNATIONAL INC. LE OTORGA /
DRA. DILIA MARIA RODRÍGUEZ D'ALEMAN Y A LA DRA. CLAUDIA LI
CARO RAMIREZ

13 \$

CERTIFICADO NOTARIAL (SOCIEDADES)

(Poderes otorgados en: El Salvador, Estados Unidos, México y Venezuela)

A los 12 días del mes de abril de 1998 el Notario que suscribe DA FE de que:

1. George C. Palek
(Nombre de la persona que firma el poder)
mayor de edad y domiciliado en Mentor, Ohio, USA firmó de su puño y letra el documento que antecede.
2. Conoce al (a la) otorgante y, que este(a) está legalmente capacitado para el otorgamiento.
3. El otorgante ha firmado el referido documento en su carácter de Presidente y Principal Ejecutivo de la persona jurídica Metal Coatings International Inc.
4. La citada persona jurídica con sede en Chardon, Ohio, USA está legalmente constituida, que tiene actualmente existencia legal y que el acto para el cual se ha otorgado este poder está comprendido entre los que constituyen su objeto social.
5. El otorgante tiene efectivamente la representación que ostenta, que esta es legítima y que está facultado para otorgar este poder.

6. Las anteriores certificaciones de los puntos 3, 4 y 5, me constan porque he tenido a la vista los documentos auténticos.

Actas de Juntas Directivas

Firma legible
Notario Público

El documento lleva un sello circular en alto relieve que reza:

SELLO NOTARIAL
ESTADO DE OHIO

Igualmente tiene un sello húmedo que lee :

BRENDA L. HAVEL
Notario Público, Estado de Ohio
Mi Comisión Vence Agosto 7, 2001
Registrado en el Condado de Ashtabula

DIANA JACOBSON S.
Traductor e Intérprete Oficial
Resolución 664 Minjusticia 1994

Diana Jacobson

14 #

5) En el ejercicio de este mandato los mandatarios arriba mencionados que facultados para: conciliar, cancelar, transigir, comprometer en árbitros, desistír recibir y tomar posesión de la cosa objeto de litigio y renunciar o desistír derechos concedidos o en curso de concesión, admitir los hechos del proceso.

6) Ratificar o no la agencia oficiosa.

7) Así mismo faculto (facultamos) a los mencionados apoderados para recibir notificaciones y designar apoderados judiciales o extrajudiciales, sustituir el presente poder y revocar las sustituciones que se hicieren.

Dado y firmado en Chardon, Ohio U.S.A.

a los 12 días del mes de mayo de 1998

(Firma ilegible)

George C. Palek, Presidente y Principal Ejecutivo

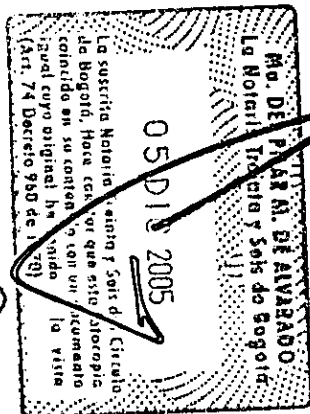
Firma

El documento lleva un sello húmedo parcial que reza :

CONSULADO GENERAL DE COLOMBIA
CHICAGO

DIANA JACOBSON S.
Traductor e Intérprete Oficial
Resolución 664 Minjusticia 1994

Diana Jacobson



No. 002106

15 \$

Yo, Carol A. Mead, Clerk de la Corte de Súplicas Ordinarias, una corte de Ley y de Inscripción del citado Condado, por este medio certifico que BRENDA L. HAVEL, ante quien se verificó o reconoció el instrumento anterior, era en la fecha de dicha verificación o reconocimiento un NOTARIO PÚBLICO, en y para el Estado, debidamente autorizado para efectuarlos y para certificar atestaciones y juramentos, y para tomar y certificar la prueba y el reconocimiento de las escrituras registradas en el Estado citado; y que conozco bien su escritura y realmente considero que la firma que aparece en los certificados citados y que se afirma como suya, es auténtica.

En fe de lo cual lo firmo y estampo el sello de la Corte citada en Jefferson, Ohio, este día 15 de mayo de 1998

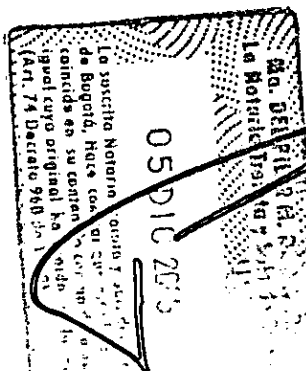
Firmado Carol A. Mead Clerk

Sigue una firma ilegible Clerk Comisionado

EL ESTADO DE OHIO
Condado de Ashtabula, ss

DIANA JACOBSON S.
Traductor e Intérprete Oficial
Resolución 664 Minjusticia 1994

Diana Jacobson



16 f

TRADUCCIÓN OFICIAL DEL PODER QUE METAL COATINGS INTERNATIONAL INC. LE OTORGA A LA DRA. DILIA MARIA RODRÍGUEZ D'ALEMAN Y A DRA. CLAUDIA LUCIA CARO RAMIREZ

PODER

Yo, (nosotros) abajo firmante(s) George C. Palek, en mi (nuestro) caracter de representante(s) legales de Metal Coatings International Inc. una sociedad organizada y existente de acuerdo con las leyes de el estado de Delaware y en actual cumplimiento de su objeto social, con domicilio en 275 Industrial Parkway Chardon, Ohio, U.S.A. por el presente instrumento confiero (conferimos) poder especial a favor de DILIA MARIA RODRIGUEZ D'ALEMAN con cédula de ciudadanía No. 41.654.882 de Bogotá, y tp 20824 y CLAUDIA LUCIA CARO RAMIREZ, con cédula de ciudadanía No. 40.017.374 de Tunja, y tp 36448, con domicilio en Santafé de Bogotá, Colombia, para que actuando en su orden en nombre del (de la) otorgante le (la) representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro de los referentes a los siguientes asuntos:

1) Solicitar, tramitar, obtener y/o registrar cualquiera de las modalidades de propiedad industrial, tales como: patentes de invención, modelos de utilidad: diseños industriales, variedades vegetales: marcas, lemas, nombres y enseñas comerciales y denominaciones de origen; así como sus renovaciones, prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.

2) Solicitar, tramitar, obtener y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how.

3) Solicitar, tramitar, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento: así como sus revocaciones o prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.

4) Ejercer acciones de oposición, observación, reclamos, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados con derechos derivados de los asuntos arriba indicados y en contra de la competencia desleal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrá(n) intervenir en juicios civiles, comerciales, penales, contencioso-administrativos, tutelas y de policía; en acciones o juicios promovidos por el (la) mandante o en contra de él (ella).

DIANA JACOBSON S.
Traductor e Intérprete Oficial
Resolución 654-Min-Justicia 1994

[Handwritten signature]



6038-1-CRC/HCS

ENCLOSURE 1

CLARKE/MODET DO BRASIL LTDA

OF OUR LETTER 93362

OF June

894

PODER

POWER OF ATTORNEY

Yo (nosotros), abajo firmante(s)

I (we), the undersigned

George C. Palek

en mi (nuestro) carácter de representante(s) legales de

legal representative(s) of

Metal Coatings International Inc.

una sociedad organizada y existente de acuerdo con las leyes de

an organization existing under the laws of

y en actual cumplimiento de su objeto social, con domicilio en

the state of Delaware

por el presente instrumento confiero (conformamos) poder especial a favor de DILIA MARIA RODRIGUEZ D'ALEMAN, con Cédula de Ciudadanía No. 41.654.882 de Bogotá, y tp. 20824 y CLAUDIA LUCIA CARO RAMIREZ, con Cédula de Ciudadanía No. 40.017.374 de Tunja, y tp. 36448, con domicilio en Santa Fé de Bogotá, Colombia, para que actuando en su orden en nombre del (de la) otorgante lo (la) representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden Administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro en lo referente a los siguientes asuntos

and in present execution of its business activity, domiciled at

275 Industrial Parkway
Chardon, Ohio, USA

do hereby grant POWER OF ATTORNEY to DILIA MARIA RODRIGUEZ D'ALEMAN, identification card No. 41.654.882 of Bogotá, and tp. 20824 and CLAUDIA LUCIA CARO RAMIREZ tp. 36448, identification card No. 40.017.374 of Tunja, residing in Santa Fé de Bogotá, Colombia, to act in the order of their appointment in behalf of grantor before any entity, authority and/or natural or juridical person, specially before those Administrative, Administrative-Contentious, Judicial, arbitration courts, and/or any other, in all matters concerning the following:

- 1) Solicitar, tramitar, obtener y/o registrar cualquiera de las modalidades de Propiedad Industrial, tales como: patentes de invención, modelos de utilidad, diseños industriales, variedades vegetales, marcas, lemas, nombres y enseñanzas comerciales y denominaciones de origen; así como sus renovaciones, prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias
- 2) Solicitar, tramitar, obtener y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how
- 3) Solicitar, tramitar, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento; así como sus renovaciones, prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias
- 4) Ejercer acciones de oposición, observación, reclamos, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados, con derechos derivados de los asuntos arriba indicados y en defensa de la competencia desleal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrá(n) intervenir en juicios civiles, comerciales, penales, contencioso-administrativos, tutelas y de policía, en acciones o juicios promovidos por el (la) mandante o en contra el (ella).
- 5) En el ejercicio de este mandato los mandatarios arriba mencionados quedan facultados para: conciliar, cancear, transigir, comprometer en arbitros, desistir, recibir y tomar posesión de la cosa, objeto de litigio y renunciar o desistir a derechos concedidos o en litigio de concesión, admitir los hechos del proceso
- 6) Ratificar o no la agencia oficiosa
- 7) Así mismo faculto (facultamos) a los mencionados apoderados para recibir notificaciones y designar apoderados judiciales o extrajudiciales, sustituir el presente poder y revocar las sustituciones que hicieron

- 1) To apply, process, obtain and/or register any of the modalities of Industrial Property, such as: Patents of Invention, Utility Models, Designs, vegetal varieties; Marks, Slogans, Trade Names and emblems and appellations of Origin; as well as their renewals, extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 2) To apply, process, obtain and/or register copyrights of any kind as well as protection of industrial secrets or know-how
- 3) To apply, process, obtain and/or register sanitary registrations, operating authorizations and/or licenses; as well as their renewals or extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 4) To bring actions of opposition, observations, claims, reconsideration, appeal or legal remedies, cancellations, nullity, protection to the consumer, granting of licenses, protection of trade secrets and other actions related with rights derived from the above-mentioned matters and against the unfair competition, actions resulting from the obtention or exploitation of licenses, recovering damages actions. They can also intervene or participate in Civil, Commercial, Criminal or Contentious-Administrative Trials, the actions for writ mandamus, police actions; in actions, lawsuits or litigations instituted by the grantor or against him.
- 5) To the effect of this mandate the above-named proxy are empowered to: conciliate, cancel, settle, submit to arbitration, withdraw and to receive and take possession of the litigation related object and waive or renounce the rights granted or in process of granting, admit the facts of the case
- 6) To ratify or not the officious agency
- 7) I (we) hereby appoint the afore mentioned attorneys with powers to receive notifications and to designate judicial and extrajudicial attorneys, substitute this Power of Attorney and to revoke such substitutions

Dado y firmado en

Granted and signed at

Chardon, Ohio, USA

a los

días de

de

on this 12th day of

May

or 1998

George C. Palek, President and CEO

Firma / signature

Recibo
de la
Cédula de Ciudadanía
No. 41.654.882 de Bogotá
y tp. 20824
y de la
Cédula de Ciudadanía
No. 40.017.374 de Tunja
y tp. 36448
Mónica





Consulado General de Colombia

500 NORTH MICHIGAN AVENUE, SUITE 2040
CHICAGO, ILLINOIS 60611

TEL (312) 923-1196 FAX (312) 923-1197

No. 728

Chicago, MAY 22 1998

El suscrito Cónsul General de Colombia, CERTIFICA, que el señor (a)

CAROL A. MEAD, quien como

SECRETARIO DE LA CORTE, autenticó la

firma del signatario del poder precedente, ejercía en la fecha las

funciones indicadas y su firma corresponde a la registrada en este

Consulado; que la compañía METAL COATINGS INTERNATIONAL, Inc.

es una sociedad constituida de acuerdo con las leyes de

○ DELAWARE y cumple su objeto conforme a las mismas;

que el (a) señor (a) GEORGE C. PALEK,

quien en su carácter de REPRESENTANTE LEGAL

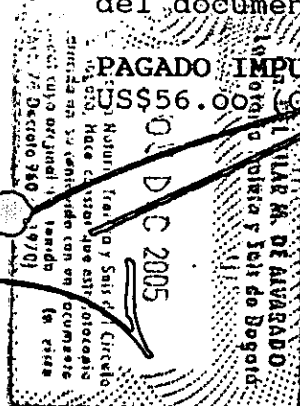
de la citada compañía confiere el poder precedente, es su

representante legal en este país.

El Cónsul General no asume responsabilidad alguna por el contenido del documento.

PAGADO IMPUESTO DE TIMBRE Y DERECHOS CONSULARES
US\$56.00 (Cincuenta y seis dólares)


CARLOS ALFONSO NEGRET MOSQUERA
Cónsul General



CERTIFICADO NOTARIAL (SOCIEDADES)
(Poderes otorgados en: El Salvador, Estados Unidos, Mexico y Venezuela)

A los _____ días del mes de _____
de _____, el Notario que suscribe DA FE de que:

1. _____
(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____

_____ firmó de su puño
y letra el documento que antecede.

2. Conoce al (a la) otorgante y que este (a) está legal-
mente capacitado para el otorgamiento.

3. El otorgante ha firmado el referido documento en su
caracter de _____

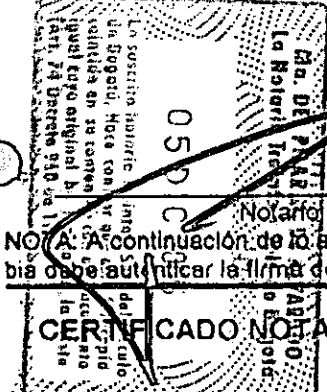
de la persona jurídica _____

4. La citada persona jurídica con sede en _____

está legalmente constituida, que tiene actualmente
existencia legal y que el acto para el cual se ha
otorgado este poder está comprendido entre los que
constituyen su objeto social.

5. El otorgante tiene efectivamente la representación que
obstenta, que esta es legítima y que está facultado
para otorgar este poder.

6. Las anteriores certificaciones de los puntos 3, 4 y 5, me
constan porque he tenido a la vista los siguientes
documentos auténticos:



NOTA: A continuación de lo anterior, el Consul de Colom-
bia debe autenticar la firma del Notario Público.

CERTIFICADO NOTARIAL (INDIVIDUOS)

A los _____ días del mes de _____
de _____, el Notario que suscribe DA FE de que:

1. _____
(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____

_____ firmó en su presencia
el documento que antecede, conoce al otorgante y que
este está legalmente capacitado para el otorgamiento.

Notario Público

NOTA: A continuación de lo anterior, el Consul de Colom-
bia debe autenticar la firma del Notario Público.

Para todos los demás países el Señor Consul de

NOTARIAL CERTIFICATE (CORPORATIONS)
(Powers of attorney granted in: El Salvador, Mexico, U.S.A. and Venezuela)

This 22nd _____ day of July, 1997,
the undersigned Notary CERTIFIES that:

1. George C. Palek
(name of the person who signs the power of attorney)

of legal age and domiciled in Mentor,

Ohio, U.S.A. set his hand on the
foregoing document.

2. The grantor is to him personally known and that he/she
has legal capacity to execute the document.

3. The grantor has executed the foregoing document in
his capacity of Treasurer & C.O.O.

of the juridical person Metal Coatings
International Inc.

4. The mentioned juridical person with place of business

in Chardon, Ohio, U.S.A.

is duly organized, has actual legal existence and that
the purposes for which the power of attorney is granted
are within the scope of its corporate purposes.

5. The grantor has in fact the referred quality and that
his/her representation is legal and that he/she is
empowered to grant this power of attorney.

6. I have based the above certifications 3, 4 and 5, on the
following authentic documents which for such purpose
were exhibited to me:

Minutes of Board of Directors Meetings

BRENDA L. HAVEL
Notary Public, State of Ohio
My Commission Expires August 7, 2001
Recorded in Ashtabula County

Brenda L. Havel
Notary Public

NOTA: Then the Colombian Consul must legalize the
signature of the Notary Public.

NOTARIAL CERTIFICATE (INDIVIDUALS)

On this _____ day of _____
the undersigned Notary CERTIFIES that:

1. _____
(name of the person who signs the Power of Attorney)

of legal age and domiciled at _____

_____ signed in his presence the
foregoing document, the grantor is to him personally known and
that he/she has legal capacity to execute the document.

Notary Public

NOTA: Then the Colombian Consul must legalize the
signature of the Notary Public.

For all other countries the Colombian Consul must

NO. 2007

20
2

I, Carol A. Mead, Clerk of the Court of Common Pleas, a court of Law and Record do hereby certify that Brenda A. Havel before whom the proof or acknowledgement of the foregoing instrument was taken signature appears to the foregoing certificate of proof or acknowledgement was at proof or acknowledgement, a NOTARY PUBLIC, in and for the State, duly authorized to take the same and certify affidavits and oaths, and to take and certify the proof and acknowledgement of deeds recorded in said State; and that I am well acquainted with his/her handwriting and verily believe that the signature to said certificate purporting to be his/hers is genuine.

County,
hose
e of said

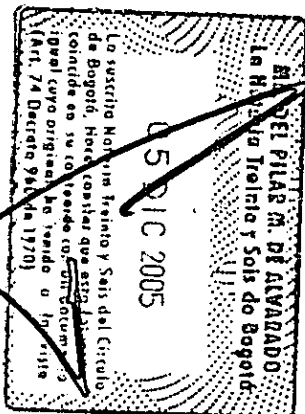
THE STATE OF OHIO
Ashtabula County, ss

In Testimony Whereof, I have hereunto set my hand and affixed the seal of said Court at Jefferson, Ohio this 31 day of July 19 97



Carol A. Mead Clerk

Deputy Clerk



21 f

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
16 December 2004 (16.12.2004)

PCT

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WO 2004/108407 A1

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C23C 22/40, 22/68, 22/82, C23F 11/00, C09K 13/04

(74) Agents: BANDY, Mark, E. et al.; Fay, Sharpe, Fagan,
Minnich & McKee, LLP, 1100 Superior Avenue, Suite 700,
Cleveland, OH 44114 (US).

(21) International Application Number:
PCT/US2004/017786

(22) International Filing Date: 4 June 2004 (04.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/476,119 5 June 2003 (05.06.2003) US

(71) Applicant (for all designated States except US): METAL
COATINGS INTERNATIONAL INC. [US/US]; 275 In-
dustrial Parkway, Chardon, OH 44024 (US).

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

(72) Inventors; and

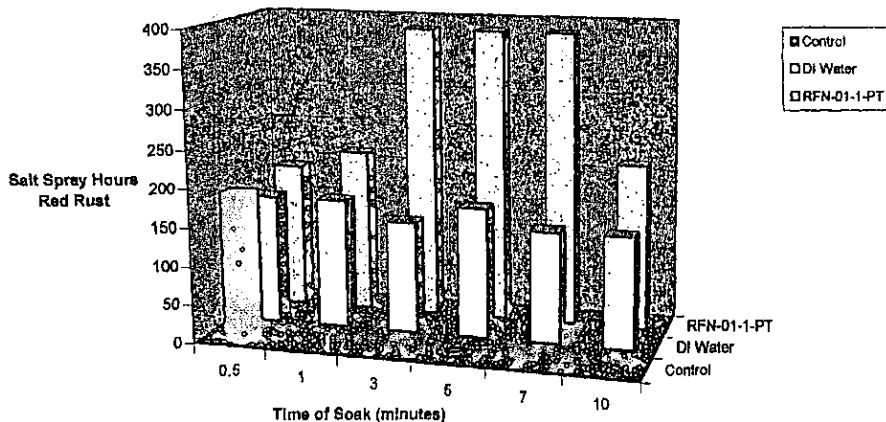
(75) Inventors/Applicants (for US only): PEARCE, Michelle,
R. [US/US]; 9810 Kite Road, Chardon, OH 44024 (US).
STRAKA, Brian, G. [US/US]; 1569 Trotter Lane,
Painesville, OH 44077 (US). GUHDE, Donald, J.
[US/US]; 160 East 191 Street, Euclid, OH 44119 (US).
DORSETT, Terry, E. [US/US]; 11205 Hosford Road,
Chardon, OH 44024 (US).

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

[Continued on next page]

(54) Title: COMPOSITIONS AND METHODS FOR DARKENING AND IMPARTING CORROSION-RESISTANT PROPERTIES TO ZINC OR OTHER ACTIVE METALS

Room Temperature Bath/Air Dry



(57) Abstract: Methods and compositions that serve to both darken a zinc or other active metal surface and impart corrosion-resistant properties thereto, are disclosed. The compositions include an aqueous solution containing about 0.1 percent to about 5 percent ammonium chloride and about 0.1 percent to about 5 percent ammonium molybdate. The compositions utilize particular ratios of concentrations of ammonium chloride and ammonium molybdate.

WO 2004/108407 A1

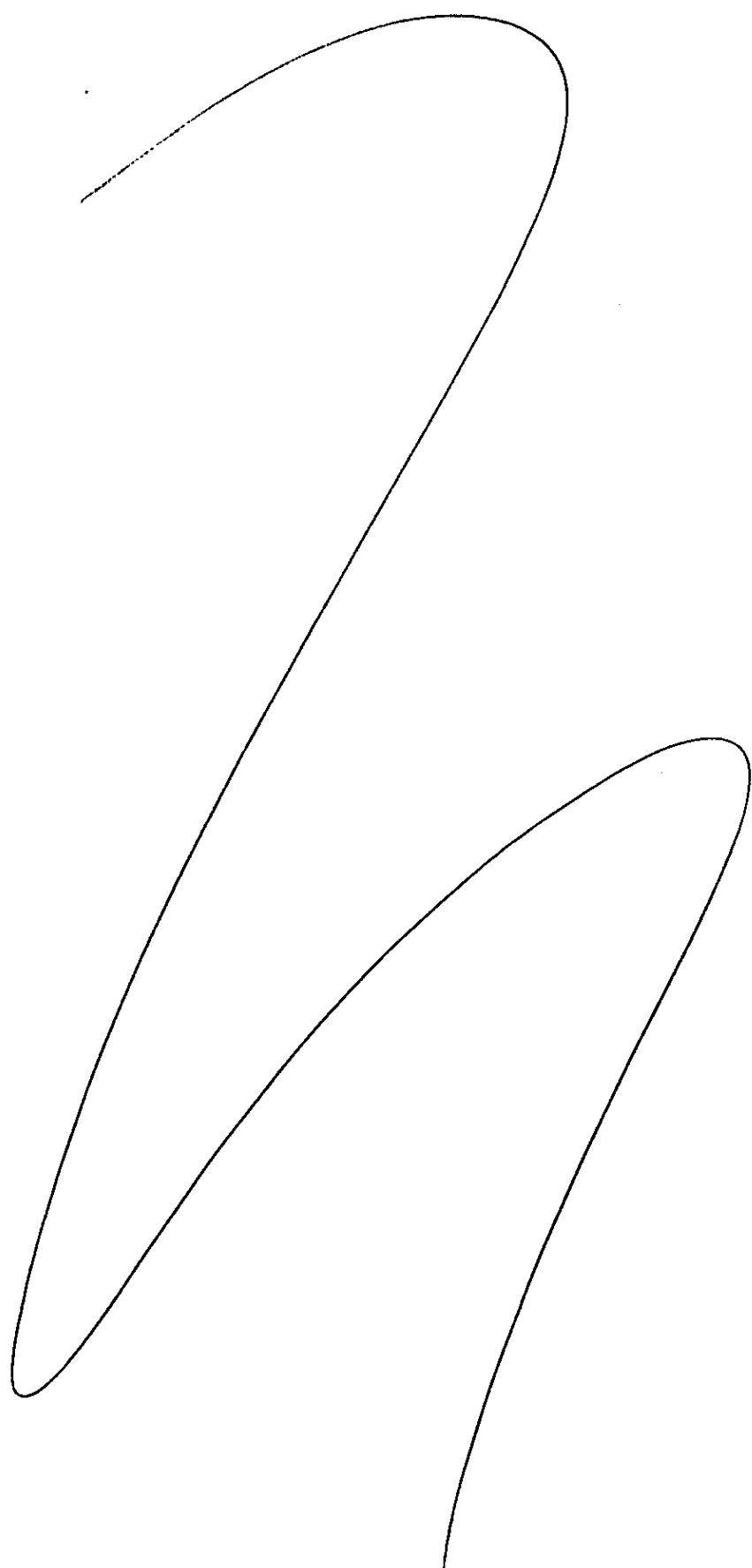
22 



Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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



23

5

**Compositions and Methods for Darkening
and Imparting Corrosion-Resistant Properties
to Zinc or Other Active Metals**

Field of the Invention

10

The present invention relates to bifunctional coatings for zinc and other active metals. The coatings serve to darken the surface of the zinc and impart anti-corrosion properties to the coated product.

Background of the Invention

15

Compositions for coating industrial components and assemblies are becoming increasingly important. For example, many mechanical parts and fasteners are coated with a composition to improve the aesthetics and overall appearance of the part or fastener, particularly when the part is visible in the final assembled product. Additionally, mechanical fasteners such as bolts or screws may be colored to simplify assembly or disassembly of a manufactured product. These compositions often contain pigments or other coloring agents as desired, to impart a certain color or appearance to the coated part.

20

Many mechanical components used in automobiles are coated with a darkening paint or composition to impart a black, gray, or dark finish. Since many mechanical components must, as a result of strength requirements, be metal; without such coatings, the metallic components are silver or at least shiny in appearance. In order to impart a black or dark appearance to such components, it is necessary to apply a suitable coating.

25

Various compositions are known for imparting a black or dark color to a metallic part. Many of these compositions are commercially available. However, for many applications, in order to effectively cover the silver and shiny metallic surface of the part, multiple coats of the coloring coating must be applied. This is undesirable because such compositions are often relatively expensive. And, multiple coating operations are labor intensive. Accordingly, there is a need for a technique to reduce the expense otherwise associated with the use of these

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35

24 \$

coloring coatings.

In addition to applying a composition to color a metallic part, other compositions are often applied to the part to impart other physical characteristics. Corrosion resistance is a desirable property for metallic parts, and particularly for such parts used in automotive applications. The art is replete with a wide variety of compositions for imparting corrosion-resistant properties to a metal surface. Coating compositions have evolved along with the changing technology of alloys and understanding of the science of corrosion.

A factor affecting the evolution of corrosion-inhibiting compositions is the relative toxicity or environmental impact of the composition or its components. For this reason, molybdate has been investigated as a suitable anti-corrosion agent, and particularly as a replacement for toxic chromium or chromium-based compounds.

Molybdenum and compounds thereof have long been recognized as corrosion inhibitors. For example, U.S. Patent 4,409,121, herein incorporated by reference, describes corrosion inhibiting compositions containing a molybdate salt. In the background section of that patent, the '121 patent notes other patents directed to corrosion inhibiting compositions containing molybdate such as U.S. Patents 4,176,059 and 4,217,216; both of which are hereby incorporated by reference.

Similarly, U.S. Patent 4,440,721, herein incorporated by reference, describes compositions for inhibiting mineral scale and corrosion in the presence of aqueous liquids. The compositions of the '721 patent include one or more water-soluble molybdate compounds. Other patents directed to aqueous compositions containing molybdenum compounds include U.S. Patents 3,030,308; 2,147,409; and 2,147,395; all of which are hereby incorporated by reference. These compositions are however, generally directed to anti-freeze compositions.

Further investigation into the corrosion inhibiting properties of molybdate led to U.S. Patent 4,548,787, herein incorporated by reference. The '787 patent describes a composition that protects against cavitation-erosion and corrosion of aluminum in aqueous liquids. That composition is based upon the combination of a phosphate and certain water-soluble agents which may include a water-soluble molybdate compound.

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Additional mention was made of the use of water-soluble salts of molybdenum in corrosion inhibiting mixtures based on a particular class of polymers, in U.S. Patent 4,640,793, herein incorporated by reference.

Perhaps the most relevant prior work in the patent literature is U.S. Patent 4,798,683, herein incorporated by reference. The '683 patent is directed to methods of controlling corrosion by the use of molybdate compositions. Specifically, the '683 patent describes methods and compositions for inhibiting the corrosion of metallic surfaces in contact with aqueous systems. The compositions of the '683 patent contain a molybdate ion source and certain water-soluble components. The '683 patent discloses molybdate ion sources as including magnesium molybdate, ammonium molybdate, lithium molybdate, sodium molybdate, and potassium molybdate.

Another interesting, although less relevant, prior work involving molybdate compositions is by Philippe Lienard and Clement Pacque entitled, "Analysis of the Mechanism of Selective Coloration Facilitating the Identification of Various Phases in Aluminum-Silicon-Copper Casting Alloys," *Homes Et Fonderie*, June-July 1982, p. 27-35. In that paper, an aqueous composition of 0.5 weight percent ammonium heptamolybdate and 3 weight percent ammonium chloride was used to emphasize and highlight grain boundaries in various alloys that were the subject of their work. There was no attempt to impart corrosion inhibiting properties to the alloys under review by the aqueous molybdate composition.

Although satisfactory in many respects, much of the prior art is directed to applications involving corrosion control in heat transfer systems and not to coating compositions for corrosion control. The two applications have significantly different criteria. Additionally, many of the prior art anti-corrosion compositions contain numerous other agents, many of which are exotic, costly, or highly toxic. Accordingly, there remains a need for a composition and method for readily imparting corrosion resistance to a metal surface. Moreover, prior art anti-corrosion compositions do not address the concerns over improving the aesthetics of metallic parts and fasteners, and particularly imparting a black or dark color to the coated part. The previously noted work by Lienard and Pacque was not directed to providing a dark surface to a metal. Moreover, Lienard and Pacque never described any aspect concerning a corrosion inhibiting composition for their

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alloy. Instead, they used the noted molybdate composition to render grain boundaries of an aluminum-silicon-copper alloy more visible, i.e. to increase the contrast between certain regions of a metal surface. Accordingly, it would be desirable to provide a composition and method for readily darkening a metallic surface. Moreover, it would be desirable to provide a composition and technique for reducing the contrast between a shiny or silvery metal surface and a dark pigmented or colored top coat. Furthermore, it would be particularly desirable to provide a composition and method for simultaneously imparting anti-corrosion, or at least corrosion-resistant properties and darkening the outer surface of a metal part.

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Summary of the Invention

In a first aspect, the present invention provides a composition comprising from about 0.1 percent to about 5 percent ammonium chloride, from about 0.1 percent to about 5 percent ammonium molybdate, and from about 90 percent to about 99.8 percent water. The composition also utilizes particular ratios of ammonium chloride to ammonium molybdate. Generally the ratio of these components is from about 1:3 to about 3:1, respectively.

In another aspect, the present invention provides an aqueous composition comprising from about 0.1 percent to about 5 percent ammonium chloride and from about 0.1 percent to about 5 percent ammonium heptamolybdate. The ratio of ammonium chloride to ammonium heptamolybdate is from about 1:3 to about 3:1.

In another aspect, the present invention provides a coated metallic substrate comprising a metal substrate having an outer surface wherein the metal is selected from the group consisting of zinc, magnesium, aluminum, manganese, and alloys thereof. The coated metallic substrate also comprises a darkening coating disposed on the substrate in which the coating is formed from an aqueous composition comprising (i) from about 0.1 percent to about 5 percent ammonium chloride, and (ii) from about 0.1 percent to about 5 percent ammonium molybdate. The ratio of ammonium chloride to ammonium molybdate is from about 1:3 to about 3:1.

In another aspect, the present invention provides a method for darkening the surface of zinc comprising providing a substrate having an outer

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surface of zinc and providing a composition including from about 0.1 percent to about 5 percent ammonium chloride and from about 0.1 percent to about 5 percent ammonium molybdate. The method also comprises a step of applying the composition to the outer surface of the zinc to form a darkening coating thereon.

5 In a further aspect, the present invention provides a method for imparting corrosion inhibiting properties to a substrate of an active metal. The method comprises providing a substrate of an active metal. The method also comprises a step of providing a composition including from about 0.1 percent to about 5 percent ammonium chloride and from about 0.1 percent to about 5 percent
10 ammonium molybdate. The ratio of ammonium chloride to ammonium molybdate is from about 1:3 to about 3:1. The method also comprises a step of applying a composition to the substrate.

In yet another aspect, the present invention provides a method for imparting corrosion resistance properties to a zinc surface. The method comprises
15 providing a component having an outer surface of zinc. The method also comprises a step of providing a composition including from about 0.1 percent to about 5 percent ammonium chloride and from about 0.1 percent to about 5 percent ammonium molybdate. The method also comprises a step of applying the composition to the outer surface of the zinc.

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Brief Description of the Drawings

Fig. 1 is a graph illustrating corrosion resistance of metal samples soaked and coated for various time periods at room temperature and air dried.

25 Fig. 2 is a graph illustrating corrosion resistance of metal samples soaked and coated for various time periods at 65°C (150°F) and air dried.

Fig. 3 is a graph illustrating corrosion resistance of metal samples soaked and coated for various time periods at room temperature and dried at 177°C (350°F).

30 Fig. 4 is a graph illustrating corrosion resistance of metal samples coated and dried at 177°C (350°F).

Fig. 5 is a comparison of metal samples coated in accordance with the present invention with uncoated, conventional samples.

Fig. 6 is another comparison of metal samples coated in accordance

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with the present invention, illustrating varying degrees of corrosion resistance.

Description of the Preferred Embodiments

The present invention provides methods and compositions for
5 darkening the surface of a metal, and particularly zinc or other active metals. The
invention also provides methods and compositions for imparting corrosion-resistant
properties to metals such as zinc or other active metals. In a most preferred
aspect, the present invention provides a composition that achieves both of these
objectives. The invention also includes the resulting coated articles or products.

10 In a preferred embodiment, the present invention provides an
aqueous solution comprising from about 0.1 percent to about 5.0 percent
ammonium chloride and from about 0.1 percent to about 5.0 percent ammonium
molybdate. All percentages noted herein are percentages by weight unless
otherwise indicated. More preferably, the aqueous solution comprises from about
15 0.5 percent to about 3.0 percent ammonium chloride and from about 0.5 percent to
about 3.0 percent ammonium molybdate. Most preferably, the aqueous solution
comprises about 2.5 percent ammonium chloride and about 2.5 percent ammonium
molybdate. It is contemplated that aqueous compositions according to the present
invention may utilize significantly higher concentrations of ammonium molybdate
20 since that component is relatively soluble in water. In contrast, ammonium chloride
is significantly less soluble in water. Regardless of the particular concentration of
ammonium chloride and ammonium molybdate utilized, it is most preferred that the
concentrations of these two components be the same or substantially so. Dual
benefits in coloring and corrosion resistance result when the concentrations of
25 these components are approximately the same. Generally, it is preferred that the
respective concentrations of these two components are from about 1:3 to about
3:1, preferably from about 1:2 to about 2:1, and most preferably about 1:1. These
ratios are weight ratios and are given with regard to the ratio of ammonium chloride
to ammonium molybdate, respectively. The balance of the preferred composition is
30 water. The present invention composition may include other additives and
components as described herein.

As previously noted, it is often desired to impart a black or dark color
to various metal components, particularly those used in the automotive industry.

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Examples of such components include, but are not limited to, fasteners, door strikes, and related assemblies. And, as previously explained, it is also desired or necessary to coat such metal components with a corrosion-resistant or corrosion inhibiting coating. The composition of the present invention may be utilized either
5 alone to provide a dark color and/or corrosion-resistant properties to a coated part, or in conjunction with one or more other coloring coatings or corrosion-resistant or corrosion inhibiting coatings. When utilized in conjunction with other coatings, the present invention composition may lead to cost savings since less of the other coating may be required, and may also provide increased corrosion resistance or
10 corrosion inhibiting characteristics. These advantages are described in greater detail herein.

The assignee of the present invention offers several commercially available corrosion-resistant coatings under the trademarks Dacromet® and Geomet®. Dacromet® is an inorganic coating based upon zinc and aluminum
15 flakes in an inorganic binder. Specific grades of Dacromet® include Dacromet 320® which contains low volatile organic compounds (VOCs); Dacromet 320 LC® which is a low chromium formulation; Dacromet 500® which is based upon the use of polytetrafluorethylene to provide consistent torque-tension characteristics; and Dacromet 320® HS which is formulated to provide a relatively thick and heavy
20 coating. Geomet® is an aqueous coating dispersion containing zinc and aluminum flakes, with an inorganic binder system. Geomet® was formulated as an alternative, environmentally friendly corrosion-resistant coating. Geomet® is water-based, low in VOCs, and free of all highly regulated toxic metals including chromium, nickel, cadmium, barium and lead. Dacromet® and Geomet® products are available from
25 Metal Coatings International, Inc., Chardon, Ohio, and also through numerous licensees thereof. Further descriptions of corrosion-inhibiting coatings are described in U.S. Patents 3,907,608; 4,555,445; 4,645,790; 4,891,268; 4,799,959; 5,006,597; 5,868,819; 6,270,884; and 6,361,872; all of which are hereby incorporated by reference.

30 If the present invention composition is used in conjunction with one or more corrosion-resistant coatings, such as previously noted or with one or more coloring or pigment-containing compositions, it is preferred to apply the present invention coating to the uncoated and exposed metal surface, prior to application of

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the corrosion-resistant coating and/or the coloring coating. Application of the present invention coating provides a base layer of a corrosion-resistant coating. In addition, the layer of the present invention composition provides a dark coloring over the metallic and often silvery or shiny appearance of the underlying metal.

5 Thus, upon subsequent application of a corrosion-resistant coating, such as a Geomet® coating, coverage is typically further improved with minimal or no indication of the metallic surface underneath. Furthermore, metallic components that are first coated with the present invention composition prior to receiving a coating of a corrosion-resistant material, generally provide a more durable and
10 longer lasting black or dark color than if only coated with the corrosion-resistant material. The reason for this is that parts not coated with the present invention composition, and only coated with a corrosion-resistant material, if scraped, often display the silvery or shiny metallic surface directly under the corrosion-resistant material. Instead, if such part is first coated with the present invention composition,
15 the coated part is black or dark in color. And so, after further application of a corrosion resistant coating, upon scraping of that part, if a region of the corrosion-resistant coating is removed, instead of the shiny metallic surface being exposed, the black or dark color of the present invention composition is exposed. This is much less noticeable as compared to the underlying metallic surface.

20 The present invention also includes methods in which the inventive compositions are applied onto the outer layer of a coated surface, such as the outer surface of a metal part previously coated with a Geomet® formulation. That is, the present invention composition may be used as a top coat or as an outer coating. Many of the parts described in the discussion of testing results herein, were first
25 coated with Geomet®, prior to application of a preferred composition according to the present invention. Significant anti-corrosion benefits resulted. Although not wishing to be bound to any particular theory, it is believed that the presence of one or more active metals in the previously deposited coating, assists in the adherence of the coating of the present invention. Therefore, for those applications in which
30 the present invention composition is applied onto a previously coated metal substrate, it is preferred that the underlying coating contain an effective amount of one or more active metals. However, it will be appreciated that the present invention includes application of the inventive compositions upon a coated metal

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substrate in which the coating does not contain any active metals.

Additionally, the present invention composition and associated methods also include strategies in which the inventive composition is used as an intermediate coating or layer. That is, the present invention composition may be applied on a coated substrate, and then one or more additional coatings applied thereon. For instance, a metal substrate may be first coated with an anti-corrosion composition such as a Geomet[®] formulation. Then, the present invention composition may be applied onto the layer of Geomet[®]. After that, one or more additional coatings or layers of other formulations may be applied on the previously applied layer of the present invention composition. Examples of additional coatings that may be applied on a previously applied layer of the present invention composition include, but are not limited to Dacrokote[®] 50 Clear, Dacrokote[®] 105, Dacrokote[®] 107, Dacrokote[®] 127, Dacrokote[®] 135, Geokote[®] 137, Geokote[®] 147, Geokote[®] 200, and Plus[®] L, all of which are commercially available from Metal Coatings International, Inc., and also through numerous licensees thereof. Descriptions of forming such multi-layer coating systems are provided in the discussion of testing results herein.

As noted, the present invention composition may be used alone or in conjunction with other compositions to provide both a dark color and corrosion protection to a metal surface. As will be appreciated, the determination of whether to use the present invention composition alone or in conjunction with one or more corrosion-resistant coatings and/or coloring compositions depends upon the application and desired properties of the coated component.

The preferred embodiment composition comprises ammonium chloride and ammonium molybdate. Although not wishing to be bound to any particular theory, it is believed that the ammonium chloride serves as an etchant to the metal surface to be coated. For example, for a zinc surface, the ammonium chloride attacks the zinc substrate and dissolves an outermost, exposed layer of zinc. The molybdate ion from the ammonium molybdate then reacts with the exposed zinc surface to form insoluble zinc molybdate or zinc molybdate oxide compounds upon the exposed zinc surface. The resulting zinc molybdate or zinc molybdate oxide compounds that are formed are believed to be passivators. The formation of these insoluble compounds creates a black or dark color. The dark

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color is a result of the mixed oxidation state of molybdate. As previously noted, the dark color renders the coated part eligible for subsequent coatings with one or more corrosion resistant coatings such as Geomet®.

Although the preferred compositions of the present invention are aqueous, the present invention includes compositions that contain one or more organic components. The term "aqueous" as used herein refers to water or water-based and includes, but is not limited to, tap water, distilled water, and deionized water. The organic component of the coating composition is preferably a low-boiling organic liquid, although there may be present some high-boiling organic liquids, so that the liquid medium may include mixtures of the foregoing. Suitable coating compositions can also be produced that contain low-boiling organic liquid, while retaining desirable composition characteristics, such as composition stability. The low-boiling organic liquids have a boiling point at atmospheric pressure below about 100°C (212°F), and are preferably water-soluble. Such low-boiling organic liquids may be represented by acetone, or low molecular weight alcohols such as methanol, ethanol, n-propylalcohol and isopropylalcohol, and further include ketones that boil below 100°C (212°F), such as water-soluble ketones, e.g., methyl ethyl ketone.

Generally, for compositions that comprise one or more organic components, the organic component will be present in an amount from about 1 to about 30 percent, basis total composition weight. Presence of such organic liquid, particularly in amounts above about 10 percent, e.g., at 15 to 25 percent, may enhance the corrosion-resistance of the coating, but use of greater than about 30 percent can become uneconomical. Preferably, for economy plus ease of composition preparation, acetone will supply the low-boiling organic liquid and will be present in an amount between about 1 and about 10 percent of the total composition. Further examples of suitable low-boiling organic liquids and high-boiling organic liquids are provided in U.S. Patents 5,868,819 and 6,270,884; both of which are herein incorporated by reference.

Yet another advantage of the present invention composition is that coatings of the composition prevent or at least significantly reduce, white corrosion products from bleeding through the coated part. For coated parts that are black or dark in color, the appearance of white corrosion is particularly noticeable and

detrimental. As will be appreciated, white corrosion or white rust is generally associated with zinc corrosion products. Red rust is generally associated with steel or iron corrosion products.

The present invention composition may comprise other compounds
5 besides or in addition to ammonium chloride and ammonium molybdate. Similarly,
other sources of molybdate ion may be used instead of or in addition to ammonium
molybdate. Examples of suitable molybdate ion sources include, but are not limited
to magnesium molybdate, lithium molybdate, sodium molybdate, potassium
molybdate, rubidium molybdate, and cesium molybdate. The term "ammonium
10 molybdate" includes ammonium dimolybdate and ammonium heptamolybdate.
Depending upon the particular application and characteristics of the solution, it is
also contemplated to utilize molybdic acid as a source, either partially or entirely, for
the molybdate ion. The specific concentration of the molybdate ion in the system
may vary depending upon the degree of hardness of the aqueous system, the
15 temperature, and the amount of dissolved oxygen in the aqueous system.

The present invention composition may also comprise additional
agents such as fluoride compounds for instance sodium fluoride, to promote
etching of the zinc surface. It is also contemplated to include one or more oxidants
or peroxides.

20 Furthermore, the present invention composition may also comprise
additional agents such as, but not limited to, wetting agents, pH modifiers,
thickeners or viscosity adjusters. Suitable wetting agents or mixture of wetting
agents can include nonionic agents such as the nonionic alkylphenol polyethoxy
adducts, for example. Also, there can be used anionic wetting agents, and these
25 are most advantageously controlled foam anionic wetting agents. Serviceable such
wetting agents or mixture of wetting agents can include anionic agents such as
organic phosphate esters, as well as the diester sulfosuccinates as represented by
sodium bistridecyl sulfosuccinate. The amount of such wetting agent is typically
present in an amount from about 0.01 to about 3 percent of the total coating
30 composition.

It is contemplated that the composition may contain a pH modifier,
which is able to adjust the pH of the final composition. Where a modifier is used,
the pH modifier is generally selected from the oxides and hydroxides of alkali

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metals, with lithium and sodium as the preferred alkali metals for enhanced coating integrity; or, it is selected from the oxides and hydroxides usually of the metals belonging to the Groups IIA and IIB in the Periodic Table, which compounds are soluble in aqueous solution, such as compounds of strontium, calcium, barium, magnesium, zinc and cadmium. The pH modifier may also be another compound, e.g., a carbonate or nitrate, of the foregoing metals.

The coating composition may also contain thickener. The thickener, when present, can contribute an amount of between about 0.01 to about 2.0 percent of thickener, basis total composition weight. This thickener can be a water-soluble cellulose ether, including the Cellosize™ thickeners. Suitable thickeners include the ethers of hydroxyethylcellulose, methylcellulose, methylhydroxypropylcellulose, ethylhydroxyethylcellulose, methylethylcellulose or mixtures of these substances. Although the cellulose ether needs to be water soluble to augment thickening of the coating composition, it need not be soluble in the organic liquid. When thickener is present, less than about 0.02 percent of the thickener will be insufficient for imparting advantageous composition thickness, while greater than about 2 percent of thickener in the composition can lead to elevated viscosities which provide compositions that are difficult to work with. Preferably, for the best thickening without deleterious elevated viscosity, the total composition will contain from about 0.1 to about 1.2 percent of thickener. It will be understood that although the use of a cellulosic thickener is contemplated, and thus the thickener may be referred to herein as cellulosic thickener, some to all of the thickener may be another thickener ingredient. Such other thickening agents include xanthan gum, associative thickeners, such as the urethane associative thickeners and urethane-free nonionic associative thickeners, which are typically opaque, high-boiling liquids, e.g., boiling above 100°C (212°F). Other suitable thickeners include modified clays such as highly beneficiated hectorite clay and organically modified and activated smectite clay, although such is not preferred. When thickener is used, it is usually the last ingredient added to the formulation.

Additionally, depending upon the application, the present invention composition may also include one or more lubricants such as, but not limited to wax; polymeric materials such as polyethylene, copolymers incorporating polyethylene, or polytetrafluorethylene; graphite; molybdenum disulfide; or

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combinations thereof.

A further advantage of the present invention composition is that, if desired, the composition may be pigment free and/or colorless prior to application to the metal surface. This feature stems from the fact that the dark color of coatings of the present invention composition after application is due to the mixed oxidation states of the resulting molybdenum compounds formed on the substrate, and not a result of pigment in the composition. Prior to application, the present invention composition is generally transparent or colorless. However, it will be appreciated that the present invention compositions may, if desired, include one or more pigments or coloring agents.

The present invention compositions and methods may be used in conjunction with a wide array of metal surfaces. For example, nearly any active metal may be coated as described herein. Preferred metals include, but are not limited to magnesium, aluminum, zinc, manganese, and alloys containing these metals. Most preferably, the metal surface to be coated in accordance with the present invention is zinc. By a "zinc" surface it is meant a surface of zinc or zinc alloy, or a metal such as steel coated with zinc or zinc alloy, as well as a substrate containing zinc in intermetallic mixture. The term "zinc" surface also includes surfaces of coatings that contain zinc or zinc compounds.

Before coating, it is in most cases advisable to remove foreign material from the substrate surface, such as by thoroughly cleaning and degreasing. Degreasing may be accomplished with known agents, for instance, with agents containing sodium metasilicate, caustic soda, carbon tetrachloride, trichlorethylene, and the like. Commercial alkaline cleaning compositions which combine washing and mild abrasive treatments can be employed for cleaning, e.g., an aqueous trisodium phosphate-sodium hydroxide cleaning solution. In addition to cleaning, the substrate may undergo cleaning plus etching, or cleaning plus hot blasting.

The present invention composition may be applied in a variety of fashions, including but not limited to dip coating, rolling, or spraying. Generally, the coating compositions may be applied by any of these various techniques, such as immersion techniques, including dip drain and dip spin procedures. Depending upon the application, the coating compositions can be applied by curtain coating,

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brush coating or roller coating and including combinations of the foregoing. It is also contemplated to use spray techniques as well as combinations, e.g., spray and spin and spray and brush techniques. Coated articles that are at an elevated temperature may be coated, often without extensive cooling, by a procedure such as dip spin, dip drain or spray coat. Depending upon the technique, several considerations should be noted. Spraying or otherwise administering the composition onto an exposed metal or coated surface is generally the simplest technique, since the composition of the feed remains constant throughout the application. In contrast, when a preset or fixed amount of the composition is used in a dip coating operation, the composition and concentration of its constituents change over time since formation of the coating is reactive in nature. For instance, upon dipping a zinc part in a bath of the present invention composition, an amount of zinc is etched or removed from the part and displaced into the bath. Concurrently, molybdate from the bath is used in the formation of the insoluble coating that forms on the exposed zinc part. And, various ammonium compounds and precipitates may form, further altering the composition of the bath. Therefore, it is preferred that controls or other monitoring methods be used to ensure that the concentration of at least the molybdate ion in the bath is maintained at an acceptable level.

After application of the coating composition to the metal or coated metal, it is preferred for best corrosion-resistance to subsequently heat-cure the applied coating. However, volatile coating substances may be initially simply evaporated from any of the applied coatings, e.g., by drying before curing. Cooling after drying may be obviated. The temperature for such drying, which may also be referred to as precuring, can be within the range from about 37°C (100°F) to about 121°C (250°F). Depending upon the application, higher temperatures may be employed. Drying times can be on the order of from about 2 to about 25 minutes, or longer.

Any elevated temperature curing of a coating composition on a substrate will often be a hot air oven cure, although other curing procedures can be used, e.g., infrared baking and induction curing. The coating composition can be heat-cured at elevated temperature, e.g., on the order of about 232°C (450°F), but usually greater, oven air temperature. The cure will typically provide a substrate

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temperature, usually as a peak metal temperature, of at least about 232°C (450°F). Oven air temperatures may be more elevated, such as on the order of 343°C (650°F) or more.

5 Curing, such as in a hot air convection oven, can be carried on for several minutes. Although cure times may be less than 5 minutes, they are more typically on the order of from at least about 10 to about 45 minutes. It is to be understood that cure times and temperatures can be effected where more than one layer of coating is applied or when there may be a subsequently applied topcoating that is a heat-cured topcoating. Thus, shorter time and lower temperature cures
10 may be employed. Also, where more than one coating is applied, or with a heat-curable topcoating, the coating may only need be dried, as discussed hereinabove. Then, curing can proceed after application of the heat-cured topcoating.

15

Testing

A series of tests were conducted to further evaluate the present invention compositions and methods. In particular, a variety of parts coated with commercially available corrosion-inhibiting compositions were compared to corresponding parts also coated with the same corrosion-inhibiting compositions
20 and further coated with a coating of the present invention. These trials are as follows.

In many of these trials, various parts and coated samples were subjected to salt sprays of varying duration. Exposure to such sprays and the effects thereof provide an insightful indication as to the corrosion resistance
25 characteristics of the part or coated sample. All salt spray testing described herein was performed in accordance with ASTM B117. Corrosion resistance of coated parts was measured by means of the standard salt spray (fog) test for paints and varnishes as set forth in ASTM B-117. In this test, the parts are placed in a chamber kept at constant temperature where they are exposed to a fine spray (fog)
30 of a 5 percent salt solution for specified periods of time, rinsed in water and dried. The extent of corrosion of the test parts can be expressed as percent of red rust.

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A. Trial No. 1

Two coats of Geomet[®] coated on 40 mm bolts as described below, were used in this first trial. The bolts were coated by placing in a wire basket and dipping the basket into the Geomet[®] coating composition, removing the basket and draining excess composition therefrom. The bolts and basket were then dip spun. During dip spinning, the basket was spun at 300 rpm for 10 seconds forward and 10 seconds reverse.

Draining was followed by baking. The bolts were placed on a sheet for baking. Baking was performed at an air temperature of about 121°C (250°F) for a time up to 10 minutes and then at 232°C (450°F) for 30 minutes. The bolts were coated twice with the coating composition using this procedure.

The Geomet[®] parts were used as the control with a coat weight of 33.7 g/m². The post-treatment used a preferred embodiment composition in accordance with the present invention, designated as RFN-01-1-PT. The formulation of this composition is set forth in Table 1, and contains 2.5 percent ammonium chloride and 2.5 percent ammonium molybdate in 95 percent water. A bath was also prepared that contained only 2.5 percent ammonium molybdate. Another bath was prepared that contained only 2.5 percent ammonium chloride. Parts were soaked in the baths for different amounts of time, ranging from 30 seconds to 10 minutes. A de-ionized water only bath and the RFN-01-1-PT bath were applied to the coated parts when the baths were at room temperature and 65°C (150°F) for comparison in salt spray. After application of the de-ionized water and RFN-01-1-PT baths, the parts were air dried 24 hours before salt spray testing. The RFN-01-1-PT bath, the 2.5 percent ammonium chloride only bath, and the 2.5 percent ammonium molybdate only bath were applied at room temperature and the parts dried for 5 minutes at 177°C (350°F). The RFN-01-1-PT bath was also applied at room temperature and 65°C (150°F) and then dried at 177°C (350°F) for 5 minutes.

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Table 1
RFN-01-1-PT

Component	Weight Percent
DI Water	95.00
Ammonium Chloride	2.50
Ammonium Molybdate	2.50
Total	100.00

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Table 2
Hours of Salt Spray
Prior to Red Rust

Soak Minutes	0	0.5	1	3	5	7	10
Room Temp Bath/Air Dry							
Control	192						
DI Water		168	168	144	168	144	144
RFN-01-1-PT		192	216	384	384	384	216
150°F Bath Temp/Air Dry							
Control	192						
DI Water		144	144	144	144	144	144
RFN-01-1-PT		504	384	384	384	312	312
Room Temp bath/350°F Dry							
Control	192						
2.5% NH4Cl		336	336	336	384	384	384
2.5% NH4MoO3		216	216	216	216	216	216
RFN-01-1-PT		384	384	528	528	384	384
350°F Dry							
Control	192						
Room Temp RFN-01-1-PT		384	384	528	528	384	384
150°F RFN-01-1-PT		384	528	384	384	384	528

10

The data in Table 2 is graphically illustrated in Figs. 1-5.

The data clearly demonstrates that post-treatment, i.e. application of the preferred embodiment composition, applied by any means improved the performance and corrosion resistance properties of Geomet® in salt spray.

15 B. Trial No. 2

In yet another series of trials, brake rotors previously coated with Geomet® were further coated with the preferred embodiment composition and subjected to various testing as follows.

20 The rotors were cleaned with acid or alkaline cleaners. The alkaline cleaned rotors were immersed in Metal Cleaner 478 alkaline cleaner for 15 minutes at 65°C (150°F). The rotors were then rinsed in tap water followed by acetone

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before application of the Geomet[®] coating. The acid cleaned rotors were first cleaned using the alkaline cleaner method listed above followed by 7 minutes in Madison Chemical Acid 162 at 48°C (120°F). The acid cleaned rotors were then rinsed in tap water followed by Madison Chemical DX 1100 de-smutter for 3 minutes at room temperature. The rotors were rinsed in tap water and then acetone prior to Geomet[®] application. The Geomet[®] was sprayed onto the rotors. The rotors were warmed in a 65°C (150°F) oven for 5 minutes before application of RFN-01-1-PT. The composition of RFN-01-1-PT is set forth in Table 1. The RFN-01-1-PT was sprayed and dip drained onto rotors. Rotors B and G were rinsed with water after applying RFN-01-1-PT. Rotors 2 and 8 were not rinsed with water following application of RFN-01-1-PT. Table 3, set forth below, lists the various rotors, manner of coating, and resulting coating thickness.

Table 3
Parts, Coatings and Film Thickness

Rotor	Coating	Film Thickness (Microns)	Deviation	Cleaning
B				Acid
Brake Surface Up		7.64	0.94	
Brake Surface Down	GEOMET and RFN-01-1-PT	7.10	0.95	
Mating Surface Up	Dip Drain RFN-01-1-PT	11.19	1.61	
G				Acid
Brake Surface Up	GEOMET and RFN-01-1-PT	8.10	0.93	
Brake Surface Down	Spray RFN-01-1-PT	7.26	1.81	
Mating Surface Up		12.16	2.02	
1				Alkaline
Brake Surface Up	GEOMET	6.03		
Brake Surface Down		6.66		
Mating Surface Up		6.64		
13				Acid
Brake Surface Up	GEOMET	6.27		
Brake Surface Down		7.63		
Mating Surface Up		6.91		
2				Alkaline
Brake Surface Up	GEOMET and RFN-01-1-PT	6.59		
Brake Surface Down	Dip Drain RFN-01-1-PT	7.54		
Mating Surface Up		7.09		
8				Alkaline
Brake Surface Up	GEOMET and RFN-01-1-PT	6.15		
Brake Surface Down	Spray RFN-01-1-PT	6.99		
Mating Surface Up		7.35		

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The coated rotors were then subjected to salt spray testing as previously described.

Table 4
Salt Spray Testing

Rotor	Salt Spray Hours						
	144	240	360	480	576	720	1004
B	5	no rust	no rust	no rust	no rust	1 to 2% rust	10% rust
G	5	no rust	no rust	no rust	no rust	< 1% rust	3% rust
1	< 1% rust	2% rust	5 to 10% rust	15 to 20% rust	pulled		
13	1 to 3% rust	5 to 10% rust	15 to 20% rust	50% rust	pulled		
2	no rust	no rust	no rust	no rust	no rust	ongoing	
8	no rust	no rust	no rust	no rust	no rust	ongoing	

The data in Table 4 is graphically illustrated in Fig. 6.

Geomet[®] rotors cleaned using alkaline cleaner produced better corrosion resistance in salt spray testing than Geomet[®] rotors cleaned in acid, with or without a post-treatment in RFN-01-1-PT. And, the data clearly demonstrates that application of the preferred embodiment composition significantly increases corrosion resistance.

C. Trial No. 3

In another series of trials, automotive door strikers were coated and tested in various fashions. Samples of strikers were coated with various commercially available coatings and were used for comparison against strikers coated in accordance with the present invention. Parts with one coat of Geomet[®] applied were also tested against parts with two coats of Geomet[®].

The preferred embodiment post-treatment solution, designated herein as RFN-01-1-PT, set forth in Table 1, was prepared for application to the door strikers coated with Geomet[®]. The treatment was applied by immersing the parts in the solution for 3 minutes, rinsing with de-ionized water, and drying with compressed air.

Parts were topcoated by a dip-spin method, at various speeds, depending on the coating. All parts were cured at 177°C (350°F) for 20 minutes, except for those coated with Dacrokote[®] 107, which were cured at 121°C (250°F) for 20 minutes. Tables 5A and 5B list the coating variations.

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Table 5A
Door Strike Coating Variations

	1 st Coat	2 nd Coat	3 rd Coat	4 th Coat
A	Geomet [®]	RFN-01-1PT	Dacrokote [®] 105	
B	Geomet [®]	RFN-01-1PT	Dacrokote [®] 105	Dacrokote [®] 105
C	Geomet [®]	RFN-01-1PT	Dacrokote [®] 107	
D	Geomet [®]	RFN-01-1PT	Dacrokote [®] 107	Dacrokote [®] 107
E	Geomet [®]	RFN-01-1PT	Geokote [®] 147	
F	Geomet [®]	RFN-01-1PT	Geokote [®] 147	Geokote [®] 147
G	Geomet [®]	RFN-01-1PT	Geokote [®] 200	
H	Geomet [®]	RFN-01-1PT	Geokote [®] 200	Geokote [®] 200
I	Geomet [®]	RFN-01-1PT		
J	Geomet [®]	RFN-01-1PT		
K	Geomet [®]	Plus [®] L		
L	Geomet [®]	RFN-01-1PT	Plus [®] L	
M	Geomet [®]	RFN-01-1PT	Dacrokote [®] 105	
N	Geomet [®]	RFN-01-1PT	Geokote [®] 200	
O	Geomet [®]	RFN-01-1PT	Plus [®] L	
P	Geomet [®]	RFN-01-1PT	Dacrokote [®] 107	
Q	Geomet [®]	RFN-01-1PT		

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Table 5B
Door Strike Coating Variations

	1 st Coat	2 nd Coat	3 rd Coat	4 th Coat	5 th Coat
R	Geomet [®]	Geomet [®]	RFN-01-1PT	Dacrokote [®] 105	
S	Geomet [®]	Geomet [®]	RFN-01-1PT	Dacrokote [®] 105	Dacrokote [®] 105
T	Geomet [®]	Geomet [®]	RFN-01-1PT	Dacrokote [®] 107	
U	Geomet [®]	Geomet [®]	RFN-01-1PT	Dacrokote [®] 107	Dacrokote [®] 107
V	Geomet [®]	Geomet [®]	RFN-01-1PT	Geokote [®] 147	
W	Geomet [®]	Geomet [®]	RFN-01-1PT	Geokote [®] 147	Geokote [®] 147
X	Geomet [®]	Geomet [®]	RFN-01-1PT	Geokote [®] 200	
Y	Geomet [®]	Geomet [®]	RFN-01-1PT	Geokote [®] 200	Geokote [®] 200
Z	Geomet [®]	Geomet [®]	RFN-01-1PT		
AA	Geomet [®]	Geomet [®]	Plus [®] L		
BB	Geomet [®]	Geomet [®]	RFN-01-1PT	Plus [®] L	
CC	Geomet [®]	Geomet [®]	RFN-01-1PT	Geokote [®] 200	
DD	Geomet [®]	Geomet [®]	RFN-01-1PT	Geokote [®] 200	Geokote [®] 200
EE	Geomet [®]	Geomet [®]	RFN-01-1PT	Plus [®] L	
FF	Geomet [®]	Geomet [®]	RFN-01-1PT		

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In summary, none of the parts with only one coat of Geomet[®] met the requirement of 360 hours in salt spray. Of those coated and treated with the preferred embodiment composition, the parts with one coat of Plus[®] L and those with one coat of Geokote[®] 200 fell 24 hours short of the requirement, with first red

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rust at 336 hours. See Table 6 for a summary of salt spray results for parts with

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one coat of Geomet®.

All of the parts with two coats of Geomet® met the 360-hour salt spray requirement, with the exception of the nontopcoated two-coat Geomet®, treated with the preferred embodiment composition, which first exhibited red rust at 216 hours. See Table 7 for the summary of two coat Geomet® parts' salt spray results.

Tables 6 and 7 contain numerical ratings corresponding to the percentage of red rust on the sample or part. The corrosion numbers in those tables indicate the extent of red rust as follows:

Percentage Red Rust	Rating
0 – Trace	5
1-5	4
6-15	3
16-25	2
26-50	1
51 +	0

All of the parts tested had at least some degree of white rust on them, the heaviest of which appeared to be on parts with the black topcoats. Parts with no topcoat had less white rusting than the black parts. Parts topcoated with Plus® L had the least white rust.

Parts coated with two coats of Geomet® significantly outperformed those with one coat of Geomet®, regardless of the topcoat, or whether treated with the preferred embodiment composition. The two-coat parts in accordance with the present invention outperformed those having commercially available coatings, but this may be due at least in part to the higher coating weight of Geomet®.

Parts from variation O (one coat Geomet®, darkening solution, and Plus® L) outperformed variation K (one coat Geomet®, no darkening solution, and Plus® L), while K outperformed variation L (one coat Geomet®, darkening solution, and Plus® L). Parts from variations BB and EE (two coats Geomet®, darkening solution, and Plus® L) outperformed parts from variation AA (two coats Geomet®, no darkening solution, and Plus® L).

Thus, it is clear that in order to meet the salt spray requirement for these parts, two coats of Geomet® are preferred. Results also indicate that the preferred embodiment composition RFN-01-1-PT improves corrosion resistance, with the one exception of variation L.

Table 6
Salt Spray Results
One Coat Geomet®

	BASE COAT(S)	TOPCOAT	SALT SPRAY HOURS											
			72	96	120	144	288	312	336	408	432	456	480	504
A	Geomet® RFN-01-1-PT	Dacrokote® 105 1110 mg/sq ft	1.5 heavy	1.0	1.0	0.0 heavy	0.0	—	—	—	—	—	—	—
B	Geomet® RFN-01-1-PT	Dacrokote® 105 1469 mg/sq ft	2.0 light	2.0	2.0	0.5 moderate	0.0	—	—	—	—	—	—	—
C	Geomet® RFN-01-1-PT	Dacrokote® 107 380 mg/sq ft	3.5 moderate		2.5	1.5 moderate	0.5	—	—	—	—	—	—	—
D	Geomet® RFN-01-1-PT	Dacrokote® 107 1089 mg/sq ft	3.0 light		3.0	1.0 moderate	0.0	—	—	—	—	—	—	—
E	Geomet® RFN-01-1-PT	Geokote® 147 422 mg/sq ft	4.0 moderate		2.0	2.0 moderate	1.0	—	—	—	—	—	—	—
F	Geomet® RFN-01-1-PT	Geokote® 147 802 mg/sq ft	4.5 light		3.5	3.0 moderate	0.5	—	—	—	—	—	—	—
G	Geomet® RFN-01-1-PT	Geokote® 200 452 mg/sq ft	4.5 moderate		4.0	4.0 moderate	2.5	—	—	—	—	—	—	—
H	Geomet® RFN-01-1-PT	Geokote® 200 966 mg/sq ft	5.0 light		4.5	4.0 light	3.0	—	—	—	—	—	—	—
J	Geomet® RFN-01-1-PT	NONE	1.5 moderate		0.0	0.0	0.0	—	—	—	—	—	—	—
K	Geomet® RFN-01-1-PT	Plus® L 545 mg/sq ft	5.0 light		5.0	5.0 light	4.5	4.5	4.5	4.0	4.0	4.0	4.0	3.0
L	Geomet® RFN-01-1-PT	Plus® L 442 mg/sq ft	3.5 light		3.0	3.0 light	2.0	—	—	—	—	—	—	—
M	Geomet® RFN-01-1-PT	Dacrokote® 105 976 mg/sq ft	5.0 heavy		4.0	3.5 heavy	2.5	—	—	—	—	—	—	—
N	Geomet® RFN-01-1-PT	Geokote® 200 966 mg/sq ft	5.0 moderate		5.0	5.0 heavy	5.0	5.0	4.0	3.5	3.0	—	—	—
O	Geomet® RFN-01-1-PT	Geokote® 200 391 mg/sq ft	5.0 light		5.0	5.0 moderate	5.0	5.0	4.5	4.5	4.5	4.0	4.0	3.5
P	Geomet® RFN-01-1-PT	Plus® L 555 mg/sq ft	5.0 moderate		4.5	4.0 heavy	3.0	—	—	—	—	—	—	—
Q	Geomet® RFN-01-1-PT	NONE	4.5 Heavy		3.5	3.5 heavy	2.5	—	—	—	—	—	—	—

Notes
A-L: Geomet applied at 14.3 g/sq m
M-Q: Geomet applied at 15.5 g/sq m
Light, Moderate, Heavy indicate degree of white rusting

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Table 7
Salt Spray Results
2 Coats Geomet®

	BASE COAT(S)	TOPCOAT	SALT SPRAY HOURS							
			216	360	384	480	504	624	792	840
R	Geomet® (2) RFN-01-1-PT	Dacrokote® 105 904 mg/sq ft	5.0 heavy	5.0	5.0	5.0	5.0	5.0	5.0	4.5 heavy
S	Geomet® (2) RFN-01-1-PT	Dacrokote® 105 1778 mg/sq ft	5.0 light	5.0	5.0	5.0	5.0	5.0	5.0	5.0 heavy
T	Geomet® (2) RFN-01-1-PT	Dacrokote® 107 483 mg/sq ft	5.0 moderate	5.0	5.0	5.0	5.0	5.0	5.0	5.0 moderate
U	Geomet® (2) RFN-01-1-PT	Dacrokote® 107 894 mg/sq ft	5 light	5.0	5.0	5.0	5.0	5.0	5.0	5.0 moderate
V	Geomet® (2) RFN-01-1-PT	Geokote® 147 391 mg/sq ft	5.0 moderate	5.0	5.0	5.0	5.0	5.0	5.0	5.0 heavy
W	Geomet® (2) RFN-01-1-PT	Geokote® 147 719 mg/sq ft	5.0 light	5.0	5.0	5.0	5.0	5.0	5.0	5.0 heavy
X	Geomet® (2) RFN-01-1-PT	Geokote® 200 473 mg/sq ft	5.0 light	5.0	5.0	5.0	5.0	5.0	5.0	5.0 heavy
Y	Geomet® (2) RFN-01-1-PT	Geokote® 200 894 mg/sq ft	5.0 light	5.0	5.0	5.0	5.0	5.0	5.0	5.0 heavy
Z	Geomet® (2) RFN-01-1-PT	NONE	5.0 moderate	5.0	5.0	5.0	5.0	4.5	4.0	4.0 moderate
AA	Geomet® Geomet®	Plus® L 493 mg/sq ft	5.0 none	5.0	5.0	5.0	4.0	3.5	3.5	3.5 light
BB	Geomet® (2) RFN-01-1-PT	Plus® L 462 mg/sq ft	5.0 light	5.0	5.0	5.0	5.0	5.0	5.0	5.0 light
CC	Geomet® (2) RFN-01-1-PT	Geokote® 200 385 mg/sq ft	5.0 moderate	5.0	4.5	4.5	4.0	3.0	2.0	1.5 heavy
DD	Geomet® (2) RFN-01-1-PT	Geokote® 200 899 mg/sq ft	5.0 heavy	5.0	5.0	4.5	4.5	4.0	2.0	2.0 heavy
EE	Geomet® (2) RFN-01-1-PT	Plus® L 411 mg/sq ft	5.0 light	5.0	5.0	5.0	5.0	4.0	3.0	3.0 light
FF	Geomet® (2) RFN-01-1-PT	NONE	4.0 moderate	2.0	2.0	1.0	1.0	0.0	0.0	0.0

Notes
R-BB: Geomet applied at 14.3 g/sq m
CC-FF: Geomet applied at 15.5 g/sq m
Light, Moderate, Heavy indicate degree of white rusting

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The foregoing description is, at present, considered to be the preferred embodiments of the present invention. However, it is contemplated that various changes and modifications apparent to those skilled in the art, may be made without departing from the present invention. Therefore, the foregoing
5 description is intended to cover all such changes and modifications encompassed within the spirit and scope of the present invention, including all equivalent aspects.

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We claim:

1. A composition comprising:
from about 0.1 percent to about 5 percent ammonium chloride;
from about 0.1 percent to about 5 percent ammonium molybdate;
5 and
from about 90 percent to about 99.8 percent water;
wherein the ratio of ammonium chloride to ammonium molybdate is
from about 1:3 to about 3:1.
- 10 2. The composition of claim 1 wherein said ratio is from about 1:2 to
about 2:1.
3. The composition of claim 1 wherein said ratio is about 1:1.
- 15 4. The composition of claim 1 wherein the concentration of
ammonium chloride is from about 0.5 percent to about 3 percent.
5. The composition of claim 1 wherein the concentration of
ammonium chloride is about 2.5 percent.
- 20 6. The composition of claim 1 wherein the concentration of
ammonium molybdate is from about 0.5 percent to about 3 percent.
7. The composition of claim 1 wherein the concentration of
25 ammonium molybdate is about 2.5 percent.
8. An aqueous composition comprising:
from about 0.1 percent to about 5 percent ammonium chloride; and
from about 0.1 percent to about 5 percent ammonium
30 heptamolybdate;
wherein the ratio of ammonium chloride to ammonium
heptamolybdate is from about 1:3 to about 3:1.

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9. The composition of claim 8 wherein said ratio is from about 1:2 to about 2:1.

10. The composition of claim 8 wherein said ratio is about 1:1.

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11. The composition of claim 8 wherein the concentration of ammonium chloride is from about 0.5 percent to about 3 percent.

12. The composition of claim 10 wherein the concentration of ammonium chloride is about 2.5 percent.

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13. The composition of claim 8 wherein the concentration of ammonium heptamolybdate is from about 0.5 percent to about 3 percent.

14. The composition of claim 10 wherein the concentration of ammonium heptamolybdate is about 2.5 percent.

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15. The composition of claim 10 comprising about 2.5 percent ammonium chloride and about 2.5 percent ammonium heptamolybdate.

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16. A coated metallic substrate comprising:

a metal substrate having an outer surface, wherein said metal is selected from the group consisting of zinc, magnesium, aluminum, manganese, and alloys and intermetallic mixtures thereof; and

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a darkening coating disposed on said substrate, said coating formed from an aqueous composition comprising (i) from about 0.1 percent to about 5 percent ammonium chloride, and (ii) from about 0.1 percent to about 5 percent ammonium molybdate, wherein the ratio of ammonium chloride to ammonium molybdate is from about 1:3 to about 3:1.

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17. The coated substrate of claim 16 further comprising:

a corrosion-resistant coating disposed on said darkening coating, wherein said corrosion-resistant coating comprises zinc flakes and aluminum

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flakes dispersed in an inorganic binder.

18. The coated substrate of claim 16 wherein said ratio is from about 1:2 to about 2:1.

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19. The coated substrate of claim 16 wherein said ratio is about 1:1.

20. The coated substrate of claim 16 wherein the concentration of ammonium chloride is from about 0.5 percent to about 3 percent.

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21. The coated substrate of claim 16 wherein the concentration of ammonium chloride is about 2.5 percent.

22. The coated substrate of claim 16 wherein the concentration of ammonium molybdate is from about 0.5 percent to about 3 percent.

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23. The coated substrate of claim 16 wherein the concentration of ammonium molybdate is about 2.5 percent.

24. The coated substrate of claim 16 wherein the concentration of ammonium chloride is about 2.5 percent and the concentration of ammonium molybdate is about 2.5 percent.

20

25. The coated substrate of claim 16 further comprising;
a corrosion-resistant coating disposed between said outer surface of said metal substrate and said darkening coating, wherein said corrosion-resistant coating comprises zinc flakes and aluminum flakes dispersed in an organic binder.

25

26. A method for darkening the surface of zinc comprising:
providing a substrate having an outer surface of zinc;
providing a composition including from about 0.1 percent to about 5 percent ammonium chloride and from about 0.1 percent to about 5 percent

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ammonium molybdate; and

applying said composition to said outer surface of said zinc to form a darkening coating thereon.

5 27. The method of claim 26 further comprising, after said step of applying said composition, a step of:

 drying said coating at a temperature of from about 37°C (100°F) to about 121°C (250°F).

10 28. The method of claim 26 further comprising, after said step of applying said composition, a step of:

 exposing said coating to a curing operation.

 29. The method of claim 26 wherein said composition comprises from
15 about 0.5 percent to about 3 percent ammonium chloride and from about 0.5 percent to about 3 percent ammonium molybdate.

 30. The method of claim 26 wherein said composition comprises about 2.5 percent ammonium chloride and about 2.5 percent ammonium molybdate.

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 31. A method for imparting corrosion inhibiting properties to a substrate of an active metal, said method comprising:

 providing a substrate of an active metal;

 providing a composition including from about 0.1 percent to about 5
25 percent ammonium chloride and from about 0.1 percent to about 5 percent ammonium molybdate, wherein the ratio of ammonium chloride to ammonium molybdate is from about 1:3 to about 3:1; and

 applying said composition to said substrate.

30 32. The method of claim 31 further comprising, after said step of applying said composition, a step of:

 drying said coating at a temperature of from about 37°C (100°F) to about 121°C (250°F).

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33. The method of claim 31 further comprising, after said step of applying said composition, a step of:
exposing said coating to a curing operation.

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34. The method of claim 31 wherein said composition comprises from about 0.5 percent to about 3 percent ammonium chloride and from about 0.5 percent to about 3 percent ammonium molybdate.

10 35. The method of claim 31 wherein said composition comprises about 2.5 percent ammonium chloride and about 2.5 percent ammonium molybdate.

36. A method for imparting corrosion resistance properties to a zinc surface, said method comprising:

15 providing a component having an outer surface of zinc;
providing a composition including from about 0.1 percent to about 5 percent ammonium chloride and from about 0.1 percent to about 5 percent ammonium molybdate; and
applying said composition to said outer surface of said zinc.

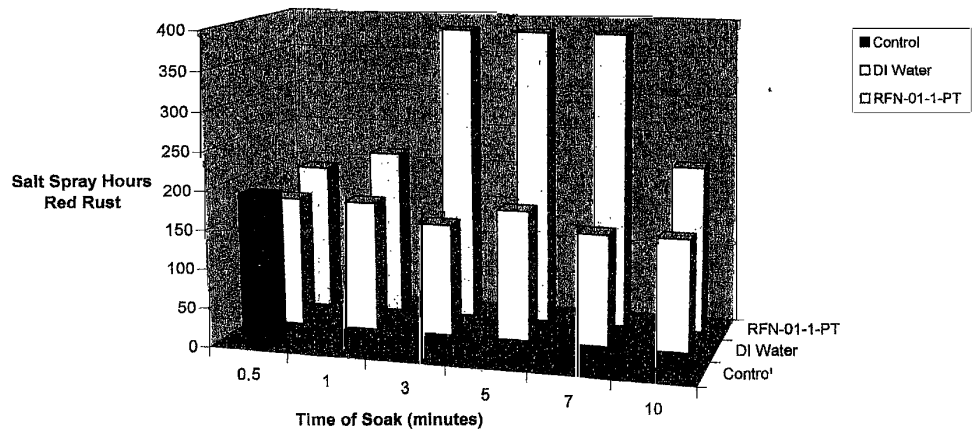
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Fig. 1
Room Temperature Bath/Air Dry

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Fig. 2
150°F Bath/Air Dry

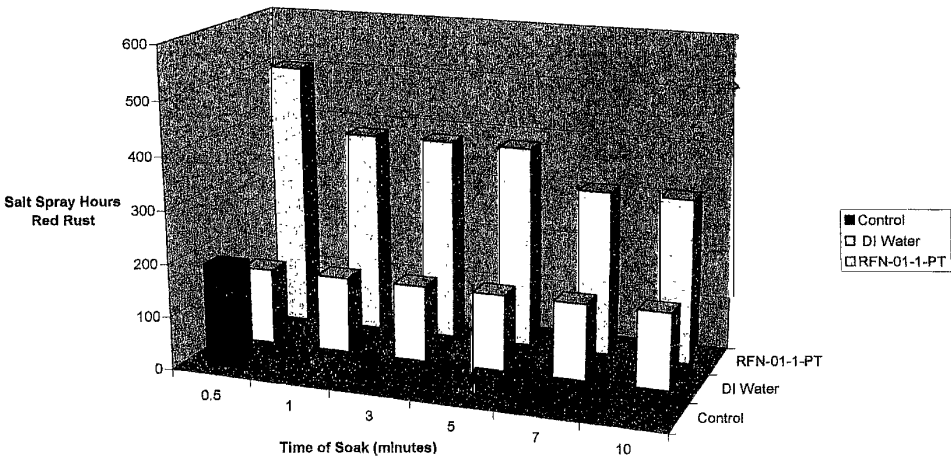


Fig. 3
Room Temperature Bath/350°F Dry

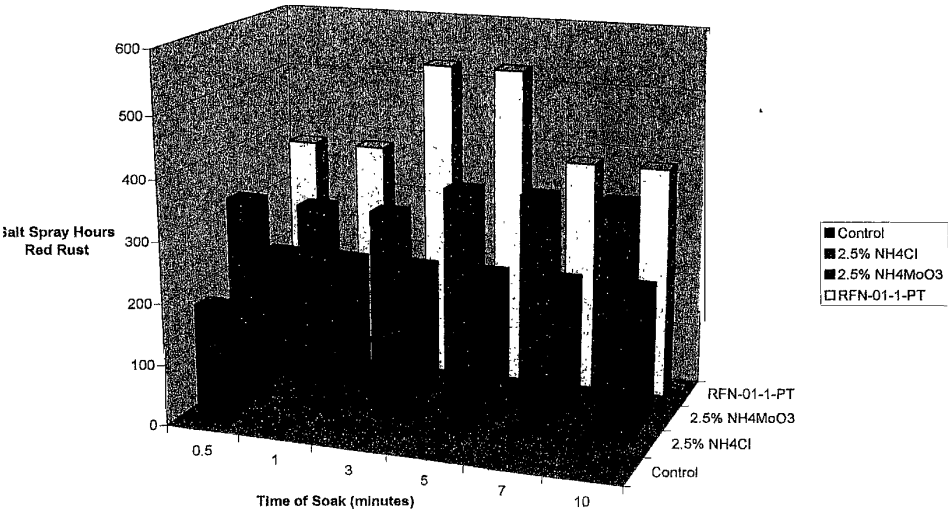


Fig. 4
RFN-01-1-PT Baked 350°F

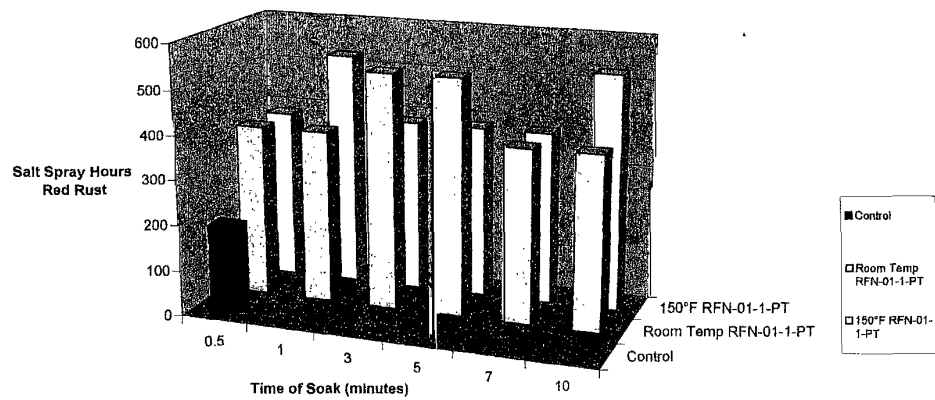


Fig. 5
Post-Treatments over GEOMET

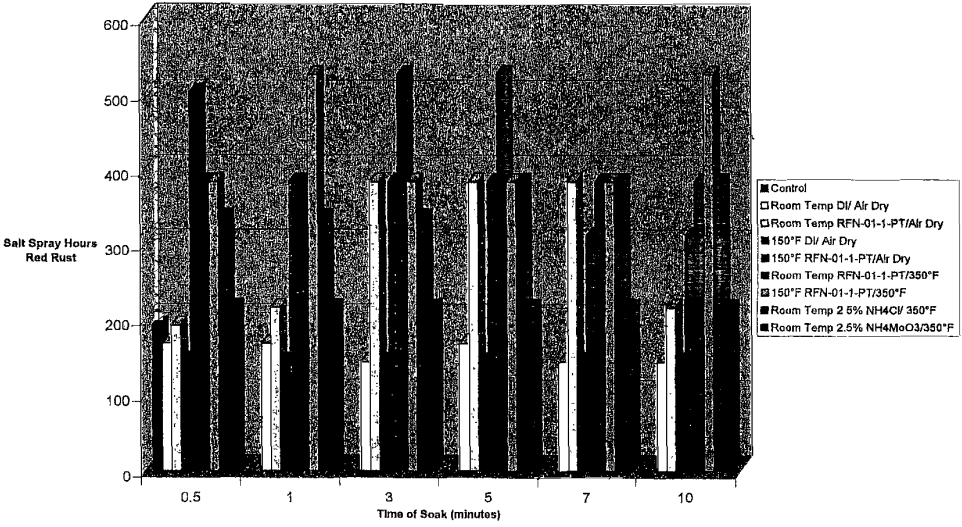
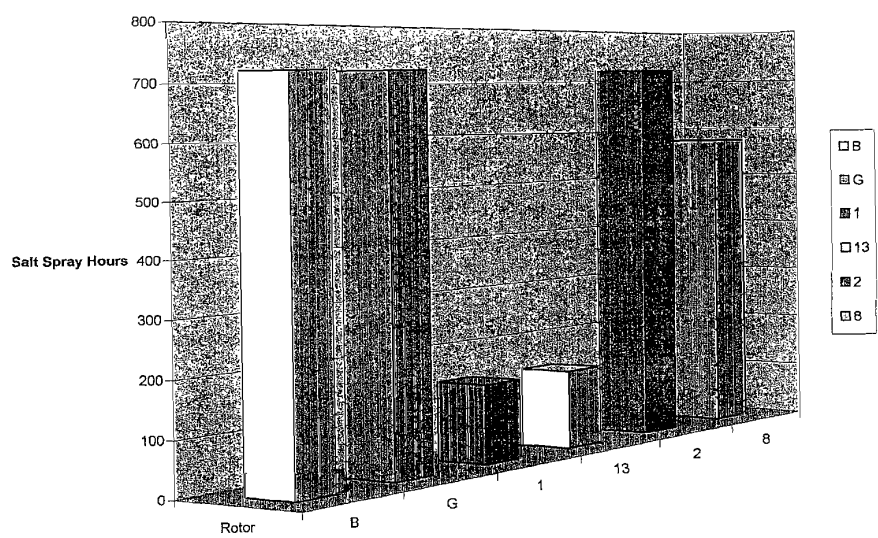


Fig. 6
First Red Rust



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**COMPOSICIONES PARA OSCURECER E IMPARTIR PROPIEDADES DE
RESISTENCIA A LA CORROSIÓN AL ZINC U OTROS METALES ACTIVOS**

La presente invención se relaciona con recubrimientos bifuncionales para zinc y otros metales activos. Los recubrimientos sirven para oscurecer la superficie del zinc e impartirle propiedades anticorrosivas al producto recubierto.

Antecedentes de la Invención

Las composiciones para recubrir componentes y montajes industriales se están volviendo crecientemente importantes. Por ejemplo, muchas partes mecánicas y aseguradores son recubiertos con una composición para mejorar la estética y la apariencia total de la parte o asegurador, particularmente cuando la parte es visible en el producto final ensamblado. Adicionalmente, los aseguradores mecánicos tal como pernos o tornillos que pueden ser coloreados para simplificar el montaje o desmontaje del producto elaborado. Estas composiciones a menudo contienen pigmentos u otros agentes colorantes según se desee para impartir un cierto color o apariencia a la parte recubierta.

Muchos componentes mecánicos utilizados en automotores son recubiertos con una pintura o composición para oscurecimiento

para impartir un acabado negro, gris u oscuro. En razón a que muchos componentes metálicos deben, como resultado de los requisitos de esfuerzo, ser de metal; sin tales recubrimientos, los componentes metálicos son en apariencia plateados o al menos brillantes. Con el fin de impartirle una apariencia blanca u oscura a tales componentes, es necesario aplicar un recubrimiento adecuado.

Varias composiciones son conocidas por impartirle un color negro u oscuro a una parte metálica. Muchas de estas composiciones están comercialmente disponibles. Sin embargo, para muchas aplicaciones, con el fin de pulir efectivamente la superficie metálica plateada y brillante de la parte, se deben aplicar múltiples recubrimientos del recubrimiento de color o del recubrimiento colorante. Esto es indeseable en razón a que tales composiciones son a menudo relativamente costosas. Y, múltiples operaciones de recubrimiento son de trabajo intensivo. De acuerdo con esto, existe la necesidad de una técnica para reducir el costo de otra manera asociado con el uso de estos agentes colorantes.

Además de aplicar una composición para colorear una parte metálica, otras composiciones son a menudo aplicadas a la parte para impartir otras características físicas. La resistencia a la corrosión es una propiedad deseable para las partes metálicas, y particularmente para tales partes

utilizadas en aplicaciones automotrices. La técnica está llena con una amplia variedad de composiciones para impartir propiedades resistentes a la corrosión a una superficie metálica. Las composiciones de recubrimiento han evolucionado junto con el cambio de la tecnología de aleaciones y el entendimiento de la ciencia de la corrosión.

Un factor que afecta la evolución de las composiciones que inhibe la corrosión es la relativa toxicidad o el impacto ambiental de las composiciones o sus componentes. Por esta razón, el molibdato ácido investigado como un agente anti-corrosión adecuado, y particularmente como un reemplazo de los compuestos tóxicos de cromo o basados en cromo.

El molibdeno y los compuestos de éstos han sido largamente reconocidos como inhibidores de la corrosión. Por ejemplo, la Patente U.S. 4,409,121, que se incorpora aquí como referencia, describe composiciones que inhiben la corrosión que contienen una sal de molibdato. En la sección de antecedentes de esa patente, la patente '121 anota otras patentes dirigidas a composiciones que inhiben la corrosión que contiene el molibdato tal como las Patentes U.S. 4,176,059 y 4,217,216; las cuales se incorporan aquí como referencia.

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De manera similar, la ~~Patente~~ U.S. 4,440,721, que se incorpora aquí como referencia, describe composiciones para inhibir el encostramiento y la corrosión mineral en la presencia de líquidos acuosos. Las composiciones de la patente '721 incluyen uno o más compuestos de molibdato solubles en agua. Otras patentes dirigidas a composiciones acuosas que contienen compuestos de molibdeno incluyen las Patentes U.S. 3,030,308; 2,147,409; y 2,147,395; todas las cuales se incorporan aquí como referencia. Estas composiciones son sin embargo, generalmente dirigidas a composiciones anti-congelamiento.

Investigaciones adicionales en las propiedades que inhiben la corrosión del molibdato conducen a la Patente U.S. 4,548,787, incorporada aquí como referencia. La Patente '787 describe una composición que protege contra la cavitación-erosión y la corrosión del aluminio en líquidos acuosos. Esa composición está basada en la combinación de un fosfato y ciertos agentes insolubles en agua que pueden incluir un compuesto de molibdato soluble en agua.

Se hace mención adicional al uso de sales solubles en agua de molibdeno en mezclas que inhiben la corrosión con base en una clase particular de polímeros, en la Patente U.S. 4,640,793, incorporada aquí como referencia.

Quizás el trabajo anterior más relevante en la literatura de patentes es la Patente U.S. 4,798,683, incorporada aquí como referencia. La Patente '683 está dirigida a métodos para controlar la corrosión mediante el uso de composiciones de molibdato. Específicamente, la patente '683 describe métodos imposiciones para inhibir la corrosión de superficies metálicas en contacto con sistemas acuosos. Las composiciones de la patente '683 contienen una fuente de ión de molibdato y ciertos componentes solubles en agua. La patente '683 describe fuentes de ión de molibdato incluyendo molibdato de magnesio, molibdato de amonio, molibdato de litio, molibdato de sodio, y molibdato de potasio.

Otro trabajo anterior interesante, aunque menos relevante, que involucra composiciones de molibdato es el de Philippe Lienard y Clement Pacque titulado, "Analysis of the Mechanism of Selective Coloration Facilitating the Identification of Various Phases in Aluminium-Silicon-Copper Casting Alloys" Home Et Fonderie, Junio-Julio 1982, p 27-35. En este documento, una composición acuosa de 0.5% de peso de heptamolibdato de amonio y 3% en peso de cloruro de amonio se utiliza para enfatizar y resaltar uniones de grano en varias aleaciones que fueron objeto de su trabajo. No hubo intento por impartir propiedades que inhibieran la corrosión a las aleaciones bajo revisión por medio de una composición de molibdato acuosa.

Aunque satisfactoria en muchos aspectos, muchas de tales técnicas anteriores están dirigidas a aplicaciones que involucran el control a la corrosión en sistemas de transferencia de calor y no a composiciones de recubrimiento para control de corrosión. Las dos aplicaciones tienen criterios significativamente diferentes. Adicionalmente, muchas de las composiciones anti-corrosión de la técnica anterior contienen otros agentes, muchos de los cuales son exóticos, costosos o altamente tóxicos. De acuerdo con esto, subsiste la necesidad de una composición y método para impartir fácilmente resistencia a la corrosión a superficie de metal. Más aún las composiciones anti-corrosión de la técnica anterior no manejan las preocupaciones sobre el mejoramiento de la estética de partes y aseguradores metálicos, y particularmente impartir un color negro u oscuro a la parte recubierta. El trabajo previamente anotado de Lienard y Pacque no está dirigido a suministrar una superficie oscura o metal. Más aún, Lienard y Pacque nunca describieron ningún aspecto concerniente a una composición que inhibiera la corrosión de su aleación. En su lugar, ellos utilizaron la composición anotada de molibdato para hacer más visible las uniones de grano de una aleación de aluminio-silicio-cobre, es decir, incrementar el contraste entre ciertas regiones de una superficie de metal. De acuerdo con esto, sería deseable suministrar una composición y método

para oscurecer fácilmente una superficie metálica. Más aún, sería deseable suministrar una composición y técnica para reducir el contraste entre una superficie metálica brillante o plateada y un recubrimiento superior pigmentado o coloreado de oscuro. Adicionalmente, sería particularmente deseable suministrar una composición y método para impartir simultáneamente anti-corrosión, y al menos propiedades de resistencia a la corrosión y oscurecimiento de la superficie exterior de una parte metálica.

Resumen de la Invención

En un primer aspecto, la presente invención suministra una composición que comprende desde aproximadamente 0.1% a aproximadamente 5% de cloruro de amonio, desde aproximadamente 0.1% a aproximadamente 5% de molibdato de amonio, y desde aproximadamente 90% a aproximadamente 99.8% de agua. La composición también utiliza proporciones particulares de cloruro de amonio a molibdato de amonio. De manera general la proporción de estos componentes va desde aproximadamente 1:3 a aproximadamente 3:1, respectivamente.

En otro aspecto, la presente invención suministra una composición acuosa que comprende desde aproximadamente 0.1% a aproximadamente 5% de cloruro de amonio y desde aproximadamente 0.1% a aproximadamente 5% de heptamolibdato

de amonio. La proporción del cloruro de amonio al heptamolibdato de amonio va desde aproximadamente 1:3 a 3:1.

En otro aspecto, la presente invención suministra un sustrato metálico recubierto que comprende un sustrato de metal que tiene una superficie exterior en donde el metal se selecciona del grupo que consiste de zinc, magnesio, aluminio, manganeso, y aleaciones de estas. El sustrato metálico recubierto también comprende un recubrimiento oscuro dispuesto sobre el sustrato en el cual está formado el recubrimiento de una composición acuosa que comprende (i) desde aproximadamente 0.1% a aproximadamente 5% de cloruro de amonio, y (ii) desde aproximadamente 0.1% a aproximadamente 5% de molibdato de amonio. La proporción del cloruro de amonio al molibdato de amonio va de 1:3 a aproximadamente 3:1.

En otro aspecto, la presente invención suministra un método para oscurecer la superficie de zinc, que comprende suministrar un sustrato que tiene una superficie exterior de zinc y suministrar una composición que incluye desde aproximadamente 0.1% a aproximadamente 5% de cloruro de amonio y desde aproximadamente 0.1% a aproximadamente 5% de molibdato de amonio. El método también comprende una etapa de aplicar la composición a la superficie exterior del zinc para formar un recubrimiento oscurecedor sobre ésta.

En un aspecto adicional, la presente invención suministra un método para impartir propiedades que inhiban la corrosión a un sustrato de un metal activo. El método comprende suministrar un sustrato de un metal activo. El método también comprende la etapa de suministrar una composición que incluye desde aproximadamente 0.1% a aproximadamente 5% de cloruro de amonio y desde aproximadamente 0.1% a aproximadamente 5% de molibdato de amonio. La proporción del cloruro de amonio al molibdato de amonio va desde aproximadamente 1:3 a aproximadamente 3:1. El método también comprende la etapa de aplicar una composición al sustrato.

En aún otro aspecto, la presente invención suministra un método para impartir propiedades de resistencia a la corrosión a una superficie de zinc. El método comprende suministrar un componente que tiene una superficie exterior de zinc. El método también comprende una etapa de suministrar una composición que incluye desde aproximadamente 0.1% a aproximadamente 5% de cloruro de amonio y desde aproximadamente 0.1% a aproximadamente 5% de molibdato de amonio. El método también comprende la etapa de aplicar la composición a la superficie exterior del zinc.

Breve Descripción de los Dibujos

La figura 1 es una gráfica que ilustra la resistencia a la corrosión de muestras de metal embebidos y recubiertos durante varios periodos de tiempo a temperatura ambiente y secados al aire.

La figura 2 es una gráfica que ilustra la resistencia a la corrosión de muestras de metal embebidas y recubiertas durante varios periodos de tiempo a 65°C (150°F) y secadas al aire.

La figura 3 es una gráfica que ilustra la resistencia a la corrosión de muestras de metal embebidas y recubiertas durante varios periodos de tiempo a temperatura ambiente y secadas a 177°C (350°F).

La figura 4 es una gráfica que ilustra la resistencia a la corrosión de muestras de metal recubiertas y secadas a 177°C (350°F).

La figura 5 es una comparación de las muestras de metal recubiertas de acuerdo con la presente invención con muestras no recubiertas, convencionales.

La figura 6 es otra comparación de las muestras de metal recubiertas de acuerdo con la presente invención, que ilustran varios grados de resistencia a la corrosión.

Descripción de las modalidades preferidas

La presente invención suministra métodos y composiciones para oscurecer la superficie de un metal, y particularmente zinc u otros metales activos. La invención también suministra métodos y composiciones para impartir propiedades de resistencia a la corrosión a metales tales como el zinc u otros metales activos. En el aspecto más preferido, la presente invención suministra una composición que logra ambos objetivos. La invención también incluye los artículos o productos recubiertos resultantes.

En una modalidad preferida, la presente invención suministra una solución acuosa que comprende desde aproximadamente 0.1% a aproximadamente 5.0% de cloruro de amonio y desde aproximadamente 0.1% a aproximadamente 5.0% de molibdato de amonio. Todos los porcentajes anotados aquí son porcentajes en peso a menos que se indique otra cosa. Más preferiblemente la solución acuosa comprende desde aproximadamente 0.5% a aproximadamente 3.0% de cloruro de amonio y desde aproximadamente 0.5% a aproximadamente 3.0% de molibdato de amonio. Más preferiblemente, la solución acuosa comprende

aproximadamente 2.5% de cloruro de amonio y aproximadamente 2.5% de molibdato de amonio. Se contempla que las composiciones acuosas de acuerdo con la presente invención puedan utilizar concentraciones significativamente mayores de molibdato de amonio en razón a que ese componente es relativamente soluble en agua. Como contraste, el cloruro de amonio es significativamente menos soluble en agua. Sin importar la concentración particular del cloruro de amonio y el molibdato de amonio utilizado, se prefiere que las concentraciones de estos dos componentes sean iguales o sustancialmente iguales. Beneficios dobles en el coloreado y la resistencia a la corrosión resultan cuando las concentraciones de estos componentes son aproximadamente iguales. En general, se prefiere que las concentraciones respectivas de estos componentes sean desde aproximadamente 1:3 a aproximadamente 3:1, preferiblemente desde aproximadamente 1:2 a aproximadamente 2:1, y más preferiblemente a aproximadamente 1:1. Las proporciones son proporciones en peso y son dadas con relación a la proporción del cloruro de amonio al molibdato de amonio, respectivamente. El balance de la composición preferida es agua. La presente composición de la invención puede incluir otros aditivos y componentes como se describen aquí.

Como se anotó previamente, se desea a menudo impartir un color negro u oscuro a varios componentes de metal,

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particularmente aquellos utilizados en la industria automotriz.

Ejemplos de tales componentes incluyen, pero no están limitados a, aseguradores, cantoneras de puertas, y montajes relacionados. Y, como se explicó previamente, también se desea o es necesario recubrir tales componentes de metal con un recubrimiento resistente a la corrosión o que inhiba la corrosión. La composición de la presente invención puede utilizar solo o suministrar un color oscuro y/o propiedades de resistencia a la corrosión a una parte recubierta, o en conjunto con uno más de otros recubrimientos colorantes o resistentes a la corrosión o recubrimientos que inhiban la corrosión. Cuando se utiliza en conjunto con otros recubrimientos, la composición de la presente invención puede conducir a ahorros en costos en razón a que se requieren menos de otros recubrimientos, y también se pueden suministrar resistencia incrementada a la corrosión o características que inhiban la corrosión. Estas ventajas son descritas con mayor detalle aquí.

El cesionario de la presente invención ofrece varios recubrimientos resistentes a la corrosión comercialmente disponibles bajo las marcas Dacromet® y Geomet®. El Dacromet® es un recubrimiento inorgánico basado en láminas de zinc y aluminio en un ligador inorgánico. Los grados específicos del

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Dacromet® incluyen Dacromet 320® que contiene compuestos orgánicos poco volátiles (VOCs); el Dacromet 320 LC® que es una formulación baja en cromo; el Dacromet 500® que está basado en el uso de politetrafluoretileno para suministrar características de torque-tensión consistentes; y el Dacromet 320® HS está formulado para suministrar un recubrimiento relativamente grueso y pesado. El Geomet® es una dispersión de recubrimiento acuoso que contiene láminas de zinc y aluminio, con un sistema inorgánico. El Geomet® fue formulado como un recubrimiento resistente a la corrosión ambientalmente amigable alternativo. El Geomet® está basado en agua, bajo en los VOC, libre de todos los metales tóxicos altamente regulados que incluyen cromo, níquel, cadmio, bario y plomo. Los productos Dacromet® y Geomet® están disponibles de Metal Coatings International Inc., Chardon, Ohio, y también a través de numerosas licencias de éstos. Las descripciones adicionales de los recubrimientos que inhibe la corrosión se describen en las patentes U.S. 3,907,608; 4,555,445; 4,645,790; 4,891,268; 4,799,959; 5,006,597; 5,868,819; 6,270,884; y 6,361,872; todos los cuales se incorporan aquí como referencia.

Si la composición de la presente invención se utiliza en conjunto con uno o más de los recubrimientos resistentes a la corrosión, tal como se anotó previamente con uno o más composiciones colorantes o que contienen pigmento, se

prefiere aplicar el recubrimiento de la presente invención en superficies de metal no recubiertos y expuestas, antes de la aplicación de el recubrimiento resistente a la corrosión y/o el recubrimiento colorante. La aplicación del recubrimiento de la presente invención suministra una capa base de o recubrimiento resistente a la corrosión. Además la capa de la composición de la presente invención suministra un colorado oscuro sobre la apariencia metálica y a menudo plateado o brillante del metal subyacente. Así, luego de la aplicación subsecuente de un recubrimiento consistente a la corrosión, tal como el recubrimiento Geomet®, el cubrimiento es típicamente mejorado adicionalmente con una indicación mínima o sin ninguna indicación de la superficie metálica inmediatamente por debajo. Adicionalmente, los componentes metálicos que son primero recubiertos con la composición de la presente invención antes de recibir un recubrimiento de un material resistente a la corrosión, generalmente suministran un color negro u oscuro durable y de larga duración que si solamente se recubriera con un material resistente a la corrosión. La razón para esto es que las partes no recubiertas con la composición de la presente invención, y solamente recubiertas con un material resistente a la corrosión, si se pelan, a menudo despliegan una superficie metálica plateada o brillante directamente bajo el material resistente a la corrosión. En su lugar, si tal parte no estuvo recubierta con la composición de la presente

invención, la parte recubierta es negra o de color oscuro. Y así, después de una aplicación adicional de un recubrimiento resistente a la corrosión, luego del pelado de la parte, si una región del recubrimiento resistente a la corrosión se remueve, en lugar de que quede una superficie metálica brillante queda expuesta, el color negro u oscuro de la composición presente invención. Esto es mucho menos notorio comparado con la superficie metálica subyacente.

La presente invención también incluye métodos los cuales las composiciones de la invención son aplicados sobre la capa exterior de una superficie recubierta, tal como la superficie exterior de una parte metálica previamente recubierta con una formulación de Geomet®. Esto es, la composición de la presente invención se puede utilizar como un recubrimiento superior o como un recubrimiento exterior. Muchas de las partes descritas en la discusión de ensayar los resultados aquí, fueron primero recubiertos con Geomet®, antes de la aplicación de una composición preferida de acuerdo con la presente invención. Se obtuvo como resultado beneficios significativos anticorrosión. Aunque no se desea estar ligado con ninguna teoría en particular, se cree que la presencia de uno o más metales activos en el recubrimiento previamente depositado, ayuda al recubrimiento de la presente invención. Por lo tanto, para aquellas aplicaciones en los cuales la composición de la presente invención se aplica sobre el

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sustrato de metal previamente recubierto, se prefiere que el recubrimiento subyacente contenga una cantidad efectiva de uno o más metales activos. Sin embargo, se apreciará que la presente invención incluye la aplicación de las composiciones de la invención sobre un sustrato de metal recubierto en el cual los recubrimientos no contengan ninguno de los metales activos.

Adicionalmente, la composición de la presente invención los métodos asociados también incluyen estrategias en los cuales la composición de la invención se utiliza como un recubrimiento capa intermedia. Esto es, la composición de la presente invención se puede aplicar sobre un sustrato recubierto, y entonces uno o más recubrimientos adicionales se aplican sobre este. Por ejemplo, un sustrato metálico puede ser primero recubierto con una composición anticorrosión tal como la formulación de Geomet®. Luego, la composición de la presente invención se puede aplicar sobre la capa de Geomet®. Después de esto uno o más recubrimientos o capas adicionales de otras formulaciones se pueden aplicar sobre la capa previamente aplicada de la composición de la presente invención. Ejemplos de recubrimientos adicionales que se pueden aplicar sobre la capa previamente aplicada de la composición de la presente invención incluye, pero no están limitados a Dacrokote® 50 Clear, Dacrokote® 105, Dacrokote® 107, Dacrokote® 127, Dacrokote® 135, Geokote® 137,

Geokote® 147, Geokote® 200, y Plus® L,m todos los cuales están comercialmente están disponibles de Metal Coatings .International, Inc., y también a través de numerosas licencias de estos. Las descripciones para formar tales sistemas de recubrimiento multicapa se suministran en la discusión de los resultados de ensayo mencionados aquí.

Como se anota, la composición de la presente invención se puede utilizar sola o en conjunto con otras composiciones para suministrar tanto un color oscuro como protección a la corrosión a una superficie metálica. Como se apreciará la determinación de si el uso de la composición de la presente invención sola en conjunto con uno o más recubrimientos resistentes a la corrosión y/o composiciones colorantes dependerá de la aplicación y las propiedades deseadas del componente recubierto.

La composición de la modalidad preferida comprende cloruro de amonio y molibdato de amonio. Aunque no se desea estar ligado por ninguna teoría particular, se cree que el cloruro de amonio sirve como un decapante para recubrir la superficie de metal. Por ejemplo, para una superficie de zinc el cloruro de amonio ataca el sustrato de zinc y disuelve la capa más exterior expuesta del zinc. El ión molibdato del molibdato de amonio reacciona con la superficie de zinc expuesta para formar compuestos de molibdato de zinc insoluble u óxido de

molibdato de zinc sobre la superficie de zinc expuesta. El molibdato de zinc resultante o los compuestos de óxido de molibdato de zinc que se forman se cree que son pasivadores. La formación de estos compuestos insolubles crean un color negro u oscuro. El color negro es el resultado de un estado de oxidación mezclada de molibdato. Como se anotó previamente, el color oscuro hace la parte recubierta elegible para recubrimientos subsecuentes con uno o más recubrimientos resistentes a la corrosión tal como el Geomet®.

Aunque las composiciones preferidas de la presente invención son acuosas, la presente invención incluye composiciones que contienen uno o más componentes orgánicos. El término "Acuoso" como se utiliza aquí se refiere a agua o materiales basados en agua e incluye, pero no están limitados a, agua de drenado, agua destilada, y agua desionizada. El componente inorgánico de la composición de recubrimiento es preferiblemente un líquido orgánico de bajo punto de ebullición, aunque pueden estar presentes algunos líquidos orgánicos de alto punto de ebullición, de tal forma que el medio líquido pueda incluir mezclas de los anteriores. Las composiciones de recubrimiento adecuadas también se pueden producir de tal forma que contengan líquidos orgánicos de bajo punto de ebullición, aunque reteniendo características de composición deseables, tales como estabilidad de

composición. Los líquidos orgánicos de bajo punto de ebullición tienen un punto de ebullición a presión atmosférica por debajo de aproximadamente 100°C (212°F), y son preferiblemente solubles en agua. Tales líquidos orgánicos de bajo punto de ebullición se pueden representar con acetona, o alcoholes de bajo peso molecular tales como metanol, etanol, n-propilalcohol e isopropilalcohol, y además incluyen cetonas que bullen por debajo de 100°C (212°F), tal como cetonas solubles en agua, por ejemplo, metil etil cetona.

Generalmente, las composiciones que comprenden uno o más componentes orgánicos, el componente orgánico estará presente en una cantidad desde aproximadamente 1 a aproximadamente 30%, de peso base total de la composición. La presencia de tal líquido orgánico, particularmente en cantidades por encima de aproximadamente 10%, por ejemplo de 10 a 25%, pueden mejorar la resistencia a la corrosión del recubrimiento, pero el uso de más de aproximadamente 30% puede ser antieconómico. Preferiblemente, para una preparación de una composición económica y fácil, la acetona suministrada en líquido orgánico de bajo punto de ebullición y estará presente en una cantidad entre aproximadamente 1 y aproximadamente 10% de la composición total. Ejemplos adicionales de líquidos orgánicos de bajo punto de ebullición y líquidos orgánicos de alto punto de ebullición se

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suministran en las patentes U.S. 5,868,819 y 6,270,884, los cuales se incorporan aquí como referencia.

Aún otra ventaja de la composición de la presente invención es que los recubrimientos de la invención evitan o al menos reducen significativamente, el sangrado de productos de corrosión blanca a través de la parte recubierta. Las partes recubiertas son negras o de color oscuro, la apariencia de la corrosión blanca es particularmente notoria y origina detrimento. Como se apreciará, la corrosión blanca o el óxido blanco está generalmente asociado con productos de corrosión de zinc. La corrosión roja está generalmente asociada con productos de corrosión de acero o hierro.

La composición de la presente invención puede comprender otros compuestos además o en adición al cloruro de amonio y al molibdato de amonio similarmente, otras fuentes de ión molibdato se pueden utilizar en lugar de o en adición al molibdato de amonio. Ejemplos de fuentes de ión de molibdato adecuado incluyen, pero no están limitadas a, molibdato de magnesio, molibdato de litio, molibdato de sodio, molibdato de potasio, molibdato de rubidio, y molibdato de cesio. El término "molibdato de amonio" incluye molibdato de amonio y heptamolibdato de amonio. Dependiendo de la aplicación particular y las características de la solución, se contempla utilizar ácido molíbdico como fuente, bien sea parcial o

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completamente, para el ión molibdato. La concentración específica del ión molibdato en el sistema puede variar dependiendo del grado de dureza del sistema acuoso, la temperatura, y la cantidad de oxígeno disuelto en el sistema acuoso.

La composición de la presente invención también puede comprender agentes adicionales tales como compuestos de flúor por ejemplo fluoruro de sodio, para promover el descapado de la superficie de zinc. También se contempla incluir uno o más oxidantes o peróxidos.

Adicionalmente, la composición de la presente invención también puede comprender agentes adicionales tales como, pero no limitados a, agentes humectantes, modificadores de pH, espesantes o ajustadores de viscosidad. Los agentes humectantes adecuados o mezclas de agentes humectantes pueden incluir agentes no biónicos tales como aductos de alquilofenol polietoxi no iónico, por ejemplo. También, se pueden utilizar agentes humectantes aniónicos de espuma ventajosamente controlados. Tales agentes o mezclas humectantes útiles de agentes humectantes pueden incluir agentes aniónicos tales como ésteres de fosfato orgánico así como el diéster o los diéster sulfosuccinatos representados por bistridecil sulfosuccinato de sodio. La cantidad de tal agente humectante está típicamente presente en una cantidad

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desde aproximadamente 0.01 a aproximadamente 3% de la composición de recubrimiento total.

Se contempla que la composición pueda contener un modificador de pH, que sea capaz de ajustar el pH de la composición final. Cuando se utiliza un modificador, el modificador de pH se selecciona generalmente de los óxidos e hidróxidos de metales alcalinos con litio y sodio como los metales alcalinos preferidos para la integridad de recubrimiento mejorado; o, se selecciona de los óxidos e hidróxidos usualmente de los metales que pertenecen a los grupos IIA y IIB de la tabla periódica, cuyos compuestos son solubles en solución acuosa, tal como compuestos de estroncio, calcio, bario, magnesio, zinc y cadmio. El modificador de pH también puede ser otro compuesto, por ejemplo, un carbonato o nitrato de los metales anteriores.

La composición de recubrimiento también puede contener un espesante. El espesante cuando está presente, puede contribuir una cantidad de entre aproximadamente 0.01% y aproximadamente 2.0% del espesante, del peso base total de la composición. Este espesante puede ser éter de celulosa soluble en agua, incluyendo los espesantes CellosizeTM. Los espesantes adecuados incluyen los éteres de hidroxietilcelulosa, metilcelulosa, metilhidroxipropilcelulosa, etilhidroxietilcelulosa

metiletilcelulosa o mezclas de estas sustancias. Aunque el éter de celulosa necesita ser soluble en agua para aumentar el espesamiento de la composición de recubrimiento, este no necesita ser soluble en líquido orgánico. Cuando el espesante está presente, menos de aproximadamente 0.002% del espesante será insuficiente para impartir espesamiento ventajoso a la composición, aunque más de aproximadamente 2% de espesante en la composición puede conducir a viscosidades elevadas que suministren composiciones que sean difíciles de trabajar o con las que sea difícil trabajar. Preferiblemente, para el mejor espesamiento sin la viscosidad deletérea elevada, la composición total concentrada desde aproximadamente 0.1 a aproximadamente 1.2% de espesante. Se entenderá que aunque se contemple el uso de un espesante celulósico, y así el espesante puede ser denominado aquí como espesante celulósico; algunos o todos los espesantes pueden ser otro ingrediente espesante. Tales otros agentes espesantes que incluyen goma de xantano, espesantes asociados, tales como espesantes asociados con uretano y espesantes asociados no iónicos libres de uretano que son líquidos típicamente opacos, de alto punto de ebullición, por ejemplo, bullen por encima de 100°C (212°F). Otros espesantes adecuados incluyen arcillas modificadas tales como arcilla hectorita altamente beneficiada y arcilla esmectita orgánicamente modificada y activada, aunque tal no se prefiere. Cuando se utiliza

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espesante, este es usualmente el último ingrediente agregado a la formulación.

Adicionalmente, dependiendo de la aplicación, la composición de la presente invención puede también incluir uno o más lubricantes tales como, pero no limitados a cera, materiales poliméricos tales como polietileno, copolímeros que incorporan polietileno, o politetrafluoroetileno, grafito. disulfuro de molibdeno; o combinaciones de estos.

Una ventaja adicional de la presente invención es que, si se desea, la composición puede ser libre de pigmento y ser incolora antes de la aplicación a la superficie de metal. Esta característica procede del hecho de que el color oscuro de los recubrimientos de la composición de la presente invención después de la aplicación se debe a los estados de oxidación mezclados de los compuestos de molibdeno resultantes sobre el sustrato, y no es un resultado del pigmento de la composición. Antes de la aplicación, la composición de la presente invención es generalmente transparente o incolora. Sin embargo, se apreciará que la composición de la presente invención puede, si se desea, incluir uno o más agentes de pigmento o colorantes.

Las composiciones y los métodos de la presente invención se pueden utilizar en conjunto con una amplia disposición de

superficies de metal. Por ejemplo, aproximadamente cualquier metal activo puede ser recubierto como se describe aquí. Los metales preferidos incluyen, pero no están limitados a magnesio, aluminio, zinc, manganeso, y aleaciones que contienen estos metales. Más preferiblemente, la superficie de metal al ser recubierta de acuerdo con la presente invención es zinc. Por una superficie "zinc" significa una superficie de zinc o aleación de zinc, o un metal como acero recubierto con zinc o aleación de zinc, así como también un sustrato que contiene zinc en mezcla intermetálica. El término superficie de "zinc" también incluye superficies de recubrimiento que contienen zinc o compuestos de zinc.

Antes del recubrimiento, es en la mayoría de los casos remover el material extraño de la superficie de sustrato, tal como al limpiar y desengrasar completamente. El desengrase se puede lograr con agentes conocidos, por ejemplo, agentes que contienen metasilicato de sodio, soda cáustica, tetracloruro de carbono, tricloroetileno, y similares. Las composiciones de limpieza alcalinas comerciales que combinan el lavado y los tratamientos abrasivos medios se pueden emplear para limpieza, por ejemplo, una producción de limpieza de fosfato de trisodio-hidróxido de sodio acuoso. Además de la limpieza, el sustrato puede sufrir limpieza más descapado, o limpieza más chorreo en caliente.

La composición de la presente invención se puede aplicar en una variedad de formas, incluyendo pero no estando limitado recubrimiento profundo, enrollado o rociado. De manera general, las composiciones de recubrimiento se pueden aplicadas por cualquiera de estas varias técnicas, tales como técnicas de inmersión, que incluyen procedimientos de giro con baño químico. Dependiendo de la aplicación, las composiciones de recubrimiento se pueden aplicar mediante recubrimiento de cortina, recubrimiento con brocha o recubrimiento con rodillo e incluyendo combinaciones de los anteriores. También se contempla utilizar técnicas de rociado así como también combinaciones, por ejemplo, técnicas de rociado y girado y rociado y brochado. Los artículos recubiertos que están a una temperatura elevada pueden ser recubiertos, a menudo sin enfriamiento extensivo, mediante un procedimiento tal como girado con baño químico, drenado con baño químico o recubrimiento por rociado. Dependiendo de la técnica, se deben anotar varias consideraciones. El rociado o la administración de otra manera de la composición sobre un metal expuesto o superficie recubierta es generalmente la técnica más simple, en razón a que la composición de la alimentación permanece constante a través de la aplicación. Como contraste, cuando una cantidad preestablecida o fija de la composición se utiliza en una operación de recubrimiento de baño químico, la composición y la concentración de sus constituyentes cambian durante el tiempo en razón a que la

formación del recubrimiento es de naturaleza reactiva. Por ejemplo, luego del baño químico una parte del baño de la composición de la presente invención, en una cantidad de zinc se descapa o se remueve de la parte y se desplaza hacia el baño. Concurrentemente, el molibdato proveniente del baño se utiliza en la formación del recubrimiento insoluble que se forma sobre la parte expuesta de zinc. Y, se pueden formar varios compuestos de amonio y precipitados, además de alterar la composición del baño. Por lo tanto, se prefiere que los controles y otros métodos de monitoreo sean utilizados para asegurar que la concentración de al menos el ión molibdato en el baño se mantenga a un nivel aceptable.

Después la aplicación de la composición de recubrimiento al metal o metal recubierto, se prefiere para una mejor resistencia a la corrosión curar por calor subsecuentemente largo el recubrimiento aplicado. Sin embargo, las sustancias de recubrimiento volátil pueden ser inicialmente simplemente evaporadas de cualquiera de los recubrimientos aplicados, por ejemplo, al secar antes de curar. El enfriar después de secado se puede obviar. La temperatura de tal secado, también puede ser denominada como un precurado, y puede estar en el rango desde aproximadamente 37°C (100°F) a aproximadamente 121°C (250°F). Dependiendo de la aplicación, se pueden emplear temperaturas mayores. Los tiempos de secado pueden

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ser del orden de aproximadamente 2 a aproximadamente 20 minutos, o mayores.

Cualquier temperatura elevada que curó la composición de recubrimiento sobre un sustrato será a menudo una cura en horno con aire caliente, aunque otros procedimientos de curación se pueden utilizar, por ejemplo, horneado infrarrojo y curado por inducción. La composición de recubrimiento puede ser curada con calor a temperatura elevada, por ejemplo, del orden de aproximadamente 232°C (450°F), pero usualmente una temperatura de aire de horno mayor. La cura típicamente suministrará temperatura de sustrato, usualmente como una temperatura metálica pico, de al menos aproximadamente 232°C (450°F). Las temperaturas de aire del horno pueden ser más elevadas, tal como del orden 343°C (650°F) o más.

El curado, tal como en un horno de convección de aire caliente, se puede llevar acabo durante varios minutos. Aunque los tiempos de curado pueden ser menor de 5 minutos, ellos son típicamente más del orden de al menos aproximadamente 10 a aproximadamente 45 minutos. Se debe entender que los tiempos de curado de las temperaturas se pueden efectuar donde se aplica más de una capa de cubrimiento o cuando puede ser subsecuentemente aplicado un recubrimiento superior que es un recubrimiento superior curado con calor. Así, tiempos más cortos y temperaturas

inferiores de curado se pueden emplear. También, cuando se aplica más de un recubrimiento, o con un recubrimiento superior curable con calor, el recubrimiento sólo necesita ser secado, con se discutió anteriormente. Entonces, el curado puede proceder después de la aplicación del recubrimiento superior curado con calor.

Ensayo

Una serie de ensayos fueron conducidos para evaluar adicionalmente las composiciones y métodos de la presente invención. En particular, una variedad de partes recubiertas con composiciones que inhibe la corrosión comercialmente disponibles se compararon con las partes correspondientes también recubiertas con las mismas composiciones que inhiben la corrosión y además recubiertas con un recubrimiento de la presente invención. Estos ensayos son como sigue.

En muchos de estos ensayos, varias partes y muestras recubiertas fueron sometidas a rociados con sal de duración variante. La exposición a tales rociados y los efectos de estos suministran una indicación perspicaz de las características de resistencia a la corrosión de la parte o muestra recubierta. Todos los ensayos con rociado con sal descritos aquí se desarrollaron de acuerdo con la ASTM B117. La resistencia a la corrosión de las partes recubiertas se



midio por medio de un ensayo con rociado con sal estandar (niebla) para pinturas y barnices como se establece en la ASTM B-117. En el ensayo, las partes estn ubicadas en una cmara mantenida a temperatura constante donde ellos son expuestos a un rociado fino (niebla) de una solucin de sal al 5% para periodos especificados de tiempo mejorada en agua y secado. La proporcin de la corrosin de las partes ensayadas se puede expresar como porcentaje de la corrosin roja.

A. Ensayo No 1

Dos capas de Geomet[®] cubiertas con pernos de 40 mm como se describe adelante, se utilizan en este primer ensayo. Los pernos se cubrieron al colocarlos en un canasto de alambre y sumergir el canasto en la composicin de recubrimiento Geomet[®], remover el canasto y drenar el exceso de composicin de este. Los pernos y el canasto son luego hilados. Durante el hilado, el canasto se hila a 3000 rpm durante 10 segundos hacia delante y 10 segundos hacia atrs.

El drenado se sustituy por el horneado. Los pernos se colocaron en una lmina para hornear. El horneado se desarroll en aire a temperatura de cerca de 121°C (250°F) durante un tiempo de hasta 10 minutos y luego a 232°C (450°F)

durante 30 minutos. Los pernos se cubrieron dos veces con la composición de recubrimiento que utiliza este procedimiento.

Las partes Geomet® se utilizaron como el control con un peso de cubierta de 33.7 g/m². El postratamiento utilizó una modalidad de la composición preferida de acuerdo con la presente invención, designada como RFN-01-1-PT. La formulación de esta composición se establece en la tabla 1, y contiene 2.5 por ciento de cloruro de amonio y 2.5 por ciento de molibdato de amonio en 95 por ciento de agua. También se preparó un baño que contiene solo 2.5 por ciento de molibdato de amonio. Otro baño se preparó y contiene solamente 2.5 por ciento de cloruro de amonio. Las partes se remojaron en baños para diferentes cantidades de tiempo, que varían de 30 segundos a 10 minutos. Solo un baño de agua desionizada y el baño de RFN-01-1-PT se aplicaron a las partes recubiertas cuando los baños estaban a temperatura ambiente y 65°C (150°F) para comparación en rociado de sal. Después de aplicación del agua desionizada y los baños de RFN-01-1-PT, las partes se secaron al aire 24 horas antes de ensayar la sal de rociado. El baño de RFN-01-1-PT, solo el baño de cloruro de amonio 2.5 por ciento, y el 2.5 por ciento de molibdato de amonio se aplicaron a temperatura ambiente y las partes se secaron durante 5 minutos a 177°C (350°F). El baño RFN-01-1-PT también se aplicó a temperatura ambiente y 65°C (150°F) y luego se secaron a 177°C (350°F) por 5 minutos.

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Tabla 1

RFN-01-1-PT

Componentes	Porcentaje en peso
Agua DE	95.00
Cloruro de amonio	2.50
Molibdato de amonio	<u>2.50</u>
Total	100.00

Tabla 2

Horas de Rociado de Sal Antes de Corrosión Roja

Minutos de enjuague	0	0.5	1	3	5	7	10
Baño a temperatura ambiente/secado al aire							
Control	192						
Agua DE		168	168	144	168	144	144
RFN-01-1-PT		192	216	384	384	384	216
Baño temperatura 150°F/secado al aire							
Control	192						
Agua DE		144	144	144	144	144	144
RFN-01-1-PT		504	384	384	384	312	312
Baño temperatura ambiente/secado 350°F							
Control	192						
2.5% NH4CL		336	336	336	384	384	384

2.5% NH ₄ MoO ₃		216	216	216	216	216	216
RFN-01-1-PT		384	384	528	528	384	384
Secado 350°F							
Control	192						
Temperatura ambiente RFN-01-1-PT		384	384	528	528	384	384
150°F RFN-01-1-PT		384	528	384	384	384	528

Los datos en la tabla 2 se ilustran gráficamente en las figuras 1-5.

Los datos demuestran claramente que el postratamiento, es decir la aplicación de la composición de la modalidad preferida aplicada por cualquier medio mejora el desempeño y las propiedades de resistencia a la corrosión del Geomet[®] en rociado de sal.

B Ensayo No 2

Aún otra serie de ensayos, rotores de frenos previamente cubiertos con Geomet[®] se cubrieron adicionalmente con la composición de la modalidad preferida y se sometieron a varios ensayos como sigue.

Los rotores se limpiaron con ácido o limpiadores alcalinos. Los rotores que se limpiaron con composiciones alcalinas se sumergieron en el limpiador de metal alcalino Metal Cleaner 478

durante 15 minutos a 65°C (150°F). Los rotores fueron luego enjuagados en un grifo de agua seguido por acetona antes de aplicación del recubrimiento Geomet®. Los rotores limpiados con ácido se limpiaron primero utilizando un método limpiador alcalino listado anteriormente seguido por 7 minutos en Madison Chemical Acid 162 a 48°C (120°F). Los rotores limpiados con ácido fueron luego enjuagados en un grifo seguido por decromado Madison Chemical DX 1100 durante 3 minutos a temperatura ambiente. Los rotores se enjuagaron en un grifo y luego se agregó acetona antes de la aplicación del Geomet®. El Geomet® se roció sobre los rotores. A 65°C (150°F) en un horno durante 5 minutos antes de aplicación del RFN-01-1-PT. La composición de RFN-01-1PT se establece en la tabla 1. El RFN-01-1-PT se roció y se drenó sobre los rotores. Los rotores B y G se enjuagaron con agua después de aplicar RFN-01-1-PT. Los rotores 2 y 8 no se enjuagaron con agua luego de la aplicación de RFN-01-1-PT. La tabla 3 que se establece adelante, lista varios rotores, forma de recubrimiento, y espesor del recubrimiento resultante.

Tabla 3

Partes, Recubrimientos y Espesor de películas

Rotor	Recubrimiento	Espesor de película (micrones)	Desviación	Limpieza
B				Ácido

Superficie de frenado para arriba		7.64	0.94	
Superficie de frenado para abajo	GEOMET y RFN-01-1-PT	7.10	0.95	
Superficie de acoplamiento para arriba	Dip Drain RFN-01-1-PT	11.19	1.61	
G				Ácido
Superficie de frenado para arriba	GEOMET y RFN-01-1-PT	8.10	0.93	
Superficie de frenado para abajo	Rociado RFN-01-1-PT	7.26	1.81	
Superficie de acoplamiento para arriba		12.16	2.02	
1				Alcalino
Superficie de frenado para arriba	GEOMET	6.03		
Superficie de frenado para abajo		6.66		
Superficie de acoplamiento para arriba		6.64		
13				Ácido
Superficie de frenado para arriba	GEOMET	6.27		
Superficie de frenado para abajo		7.63		
Superficie de acoplamiento para arriba		6.91		

2				Alcalino
Superficie de frenado para arriba	GEOMET y RFN-01-1-PT	6.59		
Superficie de frenado para abajo	Dip Drain RFN-01-1-PT	7.54		
Superficie de acoplamiento para arriba		7.09		
8				Alcalino
Superficie de frenado para arriba	GEOMET y RFN-01-1-PT	6.15		
Superficie de frenado para abajo	Rociado RFN-01-1-PT	6.99		
Superficie de acoplamiento para arriba		7.35		

Los rotores recubiertos fueron luego sometidos a ensayos de rociado como se describió previamente.

Tabla 4

Ensayo de rociado con sal

Rotor	Horas de Rociado con sal						
	144	240	360	480	576	720	1004
B	5	Sin Corrosión	Sin Corrosión	Sin Corrosión	Sin Corrosión	1 para 2% corrosión	10% corrosión
G	5	Sin Corrosión	Sin Corrosión	Sin Corrosión	Sin Corrosión	< 1% corrosión	3% corrosión
1	< 1% corrosión	2% corrosión	5 para 10% corrosión	15 para 20% corrosión	halado		
13	1	5 para	15	50%	Halado		

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	para 3% corro- sion	10% corro- sion	para 20% corro- sion	corro- sion			
2	Sin Corro sion	Sin Corros ion	Sin Corros ion	Sin Corros ion	Sin Corros ion	En curso	
8	Sin Corro sion	Sin Corros ion	Sin Corros ion	Sin Corros ion	Sin Corros ion	En curso	

Los datos en la tabla 4 se ilustran gráficamente en la Figura 6.

Los rotores Geomet® limpios que utilizan limpiador alcalino produjeron mejor resistencia a la corrosión en el ensayo de rociado de sal luego de que se limpiaron los motores con Geomet® en ácido, con o sin postratamiento en RFN-01-1-PT. y los datos demuestran claramente que la aplicación de la composición de la modalidad preferida incrementa significativamente la resistencia a la corrosión.

C Ensayo No 3

En otras series de ensayos, cantoneras de puertas de automotores se cubrieron y ensayaron en varias formas. Las muestras de las cantoneras se cubrieron con varios recubrimientos comercialmente disponibles y se utilizaron para comparación contra cantoneras cubiertas de acuerdo con la presente invención. Partes con una cubierta de Geomet®

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también se aplicaron contra partes ensayadas con dos cubiertas de Geomet®.

La solución de pretratamiento de la modalidad preferida, designada aquí como RFN-01-1-PT, se establece en la tabla 1, como se preparó para la aplicación a las cantoneras de puerta cubiertas con Geomet®. Se aplicó el tratamiento al sumergir las partes en la solución durante 3 minutos, enjuagándolas con agua desionizada, y secadas con aire comprimido.

Las partes se recubrieron mediante un método de hilado, a varias velocidades, dependiendo del recubrimiento. Todas las partes se curaron a 177°C (350°F) durante 20 minutos, excepto para aquellas que se cubrieron con Dacrokote® 107, que se curaron a 121°C (250°F) durante 20 minutos. Las tablas 5A y 5B listan las variaciones de recubrimiento.

Tabla 5A

Variaciones de Recubrimiento de Cantonera de Puerta

	1ra Capa	2da Capa	3ra Capa	4ta Capa
A	Geomet®	RFN-01-1PT	Dacrokote®105	
B	Geomet®	RFN-01-1PT	Dacrokote®105	Dracrokote®105
C	Geomet®	RFN-01-1PT	Dacrokote®107	
D	Geomet®	RFN-01-1PT	Dacrokote®107	Dracrokote®107
E	Geomet®	RFN-01-1PT	Geokote®147	

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F	Geomet®	RFN-01-1PT	Geokote®147	Geokote®147
G	Geomet®	RFN-01-1PT	Geokote®200	
H	Geomet®	RFN-01-1PT	Geokote®200	Geokote®200
I	Geomet®	RFN-01-1PT		
J	Geomet®	RFN-01-1PT		
K	Geomet®	Plus®L		
L	Geomet®	RFN-01-1PT	Plus®L	
M	Geomet®	RFN-01-1PT	Dacrokote®105	
N	Geomet®	RFN-01-1PT	Geokote®200	
O	Geomet®	RFN-01-1PT	Plus®L	
P	Geomet®	RFN-01-1PT	Dacrokote®107	
Q	Geomet®	RFN-01-1PT		

Tabla 5B

Variaciones de Recubrimiento de Cantonera de Puerta

	1ra Capa	2ra Capa	3ra Capa	4ra Capa	5ra Capa
R	Geomet®	Geomet®	RFN-01- 1PT	Dacrokote®105	
S	Geomet®	Geomet®	RFN-01- 1PT	Dacrokote®105	Dacrokote®105
T	Geomet®	Geomet®	RFN-01- 1PT	Dacrokote®107	
U	Geomet®	Geomet®	RFN-01- 1PT	Dacrokote®107	Dacrokote®107
V	Geomet®	Geomet®	RFN-01- 1PT	Geokote®147	
W	Geomet®	Geomet®	RFN-01- 1PT	Geokote®147	Geokote®147
X	Geomet®	Geomet®	RFN-01- 1PT	Geokote®200	
Y	Geomet®	Geomet®	RFN-01- 1PT	Geokote®200	Geokote®200
Z	Geomet®	Geomet®	RFN-01-		

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			1PT		
AA	Geomet®	Geomet®			
BB	Geomet®	Geomet®	RFN-01- 1PT	Plus®L	
CC	Geomet®	Geomet®	RFN-01- 1PT	Geokote®200	
DD	Geomet®	Geomet®	RFN-01- 1PT	Geokote®200	Geokote®200
EE	Geomet®	Geomet®	RFN-01- 1PT	Plus®L	
FF	Geomet®	Geomet®	RFN-01- 1PT		

En resumen, ninguna de las partes con solo una cubierta de Geomet® cumple con los requerimientos de 366 horas de rociado con sal. De aquellas cubiertas y tratadas con la composición de la modalidad preferida, las partes con una cubierta de Plus®L y aquellas con una cubierta de Geokote® 200 caen dentro de las 24 horas del requerimiento con la primera corrosión roja a 336 horas. Ver tabla 6 para un resumen de los resultados de rociado de sal para las partes con un recubrimiento Geomet®.

Todas las partes con dos recubrimientos de Geomet® cumplen con los requerimientos de rociado de sal de 360 horas, con la excepción de las dos cubiertas Geomet® no recubiertas en la parte superior, tratadas con la composición de la modalidad preferida, que primero exhibe corrosión roja a 216 horas. Ver

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tabla 7 para el resumen de los resultados de rociado de sal de las dos partes Geomet® de capa.

Las tablas 6 y 7 contienen proporciones numéricas que corresponden al porcentaje de corrosión roja en la muestra o parte. Los números de corrosión en aquellas tablas indican el alcance de la corrosión roja como sigue:

<u>Porcentaje de corrosión</u> <u>roja</u>	<u>Grado</u>
0-traza	5
1-5	4
6-15	3
16-25	2
26-50	1
51+	0

Todas las partes ensayadas tienen al menos un grado de corrosión sobre ellas, el más pesado de los cuales parece estar en las partes con recubrimientos superiores negros, las partes con recubrimiento superior tienen menos corrosión blanca que las partes negras. Las partes superiores cubiertas con Plus®L tienen al menos corrosión blanca.

Las partes cubiertas con dos capas de Geomet® superó significativamente aquellas con una capa de Geomet®, con respecto a la cubierta superior, o si se trata con la

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composición de la modalidad preferida. Las dos partes de cubierta de acuerdo con la presente invención superaron aquellas que tienen recubrimientos disponibles comercialmente, pero esta se puede deber al menos en parte al mayor peso de recubrimiento del Geomet®.

Partes de variación O (una cubierta Geomet®, solución de oscurecimiento y Plus®L) superaron la variación K (una cubierta Geomet®, solución no oscurecida y plus®L) mientras K supera la variación L (una cubierta Geomet®, solución de oscurecimiento, y Plus®L). Las partes de las variaciones BB y EE (dos cubiertas Geomet®, solución de oscurecimiento, y Plus®L) superaron partes de la variación AA (dos cubiertas Geomet®, sin solución de oscurecimiento, y Plus®L).

Así, es claro que cumplir los requerimientos de rociado de sal para estas partes, se prefieren dos capas de Geomet®. Los resultados también indican que la composición de la modalidad preferida RFN-01-1-PT mejora la resistencia de la corrosión, con una excepción de la variación L.

Tabla 6
Resultados de Rociado con Sal
Una Capa Geomet®

Horas de rociado de sal														
	Capa base (s)	Capa superior	72	96	120	144	288	312	336	408	432	456	480	504
A	Geomet® RFN-01- 1-PT	Dacrokote®105 1110 mg/sq ft	1.5 pesado	1.0	1.0	0.0 pesado	0.0	—	—	—	—	—	—	—
B	Geomet® RFN-01- 1-PT	Dacrokote®105 1469 mg/sq ft	2.0 liviano	2.0	2.0	0.5 moderado	0.0	—	—	—	—	—	—	—
C	Geomet® RFN-01- 1-PT	Dacrokote®107 380 mg/sq ft	3.5 moderado		2.5	1.5 moderado	0.5	—	—	—	—	—	—	—
D	Geomet® RFN-01- 1-PT	Dacrokote®107 1089 mg/sq ft	3.0 liviano		3.0	1.0 moderado	0.0	—	—	—	—	—	—	—
E	Geomet® RFN-01- 1-PT	Geokote®147 422 mg/sq ft	4.0 moderado		2.0	2.0 moderado	1.0	—	—	—	—	—	—	—
F	Geomet® RFN-01- 1-PT	Geokote®147 802 mg/sq ft	4.5 Liviano		3.5	3.0 moderado	0.5	—	—	—	—	—	—	—
G	Geomet® RFN-01- 1-PT	Geokote®200 452 mg/sq ft	4.5 moderado		4.0	4.0 moderado	2.5	—	—	—	—	—	—	—
H	Geomet® RFN-01-	Geokote®200 966 mg/sq ft	5.0 liviano		4.5	4.0 liviano	3.0	—	—	—	—	—	—	—

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	1-PT													
J	Geomet® RFN-01- 1-PT	Ninguno	1.5 moderado		0.0	0.0	0.0	—	—	—	—	—	—	—
K	Geomet®	Plus® L 545 mg/sq ft	5.0 liviano		5.0	5.0 liviano	4.5	4.5	4.5	4.0	4.0	4.0	4.0	3.0
L	Geomet® RFN-01- 1-PT	Plus® L 442 mg/ sq ft	3.5 liviano		3.0	3.0 liviano	2.0	—	—	—	—	—	—	—
M	Geomet® RFN-01- 1-PT	Dacrokote®105 976 mg/sq ft	5.0 pesado		4.0	3.5 pesado	2.5	—	—	—	—	—	—	—
N	Geomet® RFN-01- 1-PT	Geokote®200 966 mg/sq ft	5.0 moderado		5.0	5.0 pesado	5.0	5.0	4.0	3.5	3.0			
O	Geomet® RFN-01- 1-PT	Geokote®200 391 mg/sq ft	5.0 liviano		5.0	5.0 moderado	5.0	5.0	4.5	4.5	4.5	4.0	4.0	3.5
P	Geomet® RFN-01- 1-PT	Plus® L 555 mg/sq ft	5.0 moderado		4.5	4.0 pesado	3.0	—	—	—	—	—	—	—
Q	Geomet® RFN-01- 1-PT	Ninguno	4.5 pesado		3.5	3.5 pesado	2.5	—	—	—	—	—	—	—

Notas

A-L: Geomet aplica en 14.3 g/sq m
M-Q: Geomet aplica en 15.5 g/sq m
Liviano, moderado, pesado indican el grado del corrosión blanco

Tabla 7
Resultados de Rociado con Sal
2 Capas Geomet®

HORAS DE ROCIADO CON SAL										
	Capa base	Capa superior	216	360	384	480	504	624	792	840
R	Geomet® (2) RFN- 01-1-PT	Dacrokote®105 904 mg/sq ft	5.0 pesado	5.0	5.0	5.0	5.0	5.0	5.0	4.5 pesado
S	Geomet® (2) RFN- 01-1-PT	Dacrokote®105 1778 mg/sq ft	5.0 liviano	5.0	5.0	5.0	5.0	5.0	5.0	5.0 pesado
T	Geomet® (2) RFN- 01-1-PT	Dacrokote®107 483 mg/sq ft	5.0 moderado	5.0	5.0	5.0	5.0	5.0	5.0	5.0 moderado
U	Geomet® (2) RFN- 01-1-PT	Dacrokote®107 894 mg/sq ft	5.0 liviano	5.0	5.0	5.0	5.0	5.0	5.0	5.0 moderado
V	Geomet® (2) RFN-	Geokote®147 391 mg/sq ft	5.0 moderado	5.0	5.0	5.0	5.0	5.0	5.0	5.0 pesado

	01-1-PT									
W	Geomet® (2) RFN- 01-1-PT	Geokote®147 719 mg/sq ft	5.0 liviano	5.0	5.0	5.0	5.0	5.0	5.0	5.0 pesado
X	Geomet® (2) RFN- 01-1-PT	Geokote®200 473 mg/sq ft	5.0 liviano	5.0	5.0	5.0	5.0	5.0	5.0	5.0 pesado
Y	Geomet® (2) RFN- 01-1-PT	Geokote®200 894 mg/sq ft	5.0 liviano	5.0	5.0	5.0	5.0	5.0	5.0	5.0 pesado
Z	Geomet® (2) RFN- 01-1-PT	Ninguno	5.0 moderado	5.0	5.0	5.0	5.0	4.5	4.0	4.0 moderado
AA	Geomet® Geomet®	Plus® L 493 mg/sq ft	5.0 ninguno	5.0	5.0	5.0	4.0	3.5	3.5	3.5 liviano
BB	Geomet® (2) RFN- 01-1-PT	Plus® L 462 mg/sq ft	5.0 liviano	5.0	5.0	5.0	5.0	5.0	5.0	5.0 liviano
CC	Geomet® (2) RFN- 01-1-PT	Geokote®200 385 mg/sq ft	5.0 moderado	5.0	4.5	4.5	4.0	3.0	2.0	1.5 pesado

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DD	Geomet® (2) RFN- 01-1-PT	Geokote®200 899 mg/sq ft	5.0 pesado	5.0	5.0	4.5	4.5	4.0	2.0	2.0 pesado
EE	Geomet® (2) RFN- 01-1-PT	Plus® L 411 mg/sq ft	5.0 liviano	5.0	5.0	5.0	5.0	4.0	3.0	3.0 liviano
FF	Geomet® (2) RFN- 01-1-PT	Ninguno	4.0 moderado	2.0	2.0	1.0	1.0	0.0	0.0	0.0

Notas

R-BB: Geoment aplica en 14.3 g/sq m

CC-FF: Geoment aplica en 15.5 g/sq m

Liviano, moderado, pesado indican el grado de corrosión blanco.

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La anterior descripción, se considerada actualmente la modalidad preferida de la presente invención. Sin embargo, se contempla que varios cambios y modificaciones evidentes para aquellos expertos en la técnica, pueden ser hechas sin apartarse de la presente invención. Por lo tanto, la anterior descripción se pretende cubra todos tales cambios y modificaciones abarcados dentro del espíritu y alcance de la siguiente invención, que incluye todos los aspectos equivalentes

REIVINDICACIONES

Reivindicamos:

1. Una composición que comprende:

De cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio;

De cerca de 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio;

y

Cerca de 90 por ciento a cerca de 99,8 por ciento de agua; en donde la proporción de cloruro de amonio para el molibdato de amonio es cerca de 1:3 a 3:1.

2. La composición de la reivindicación 1 en donde dicha proporción es de 1:2 a cerca de 2:1.

3. La composición de la reivindicación 1 en donde dicha proporción es de 1:1

4. La composición de la reivindicación 1 en donde la concentración de cloruro de amonio es de 0,5 por ciento a cerca de 3 por ciento

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100

5. La composición de la reivindicación 1 en donde la concentración de cloruro de amonio es de cerca de 2,5 por ciento

6. La composición de la reivindicación 1 en donde la concentración de molibdato de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.

7. La composición de la reivindicación 1 en donde la concentración de molibdato de amonio es cerca de 2,5 por ciento.

8. Una composición acuosa comprende:

De cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio; y de cerca de 0,1 por ciento a cerca de 5 por ciento de heptamolibdato de amonio;

En donde la proporción de cloruro de amonio para el heptamolibdato de amonio es cerca de 1:3 a cerca de 3:1.

9. La composición de la reivindicación 8 en donde dicha proporción es de 1:2 a cerca de 2:1.

10. La composición de la reivindicación 8 en donde dicha proporción es de 1:1

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11. La composición de la reivindicación 8 en donde la concentración de cloruro de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.
12. La composición de la reivindicación 10 en donde la concentración de cloruro de amonio es de cerca de 2,5 por ciento.
13. La composición de la reivindicación 8 en donde la concentración de heptamolibdato de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.
14. La composición de la reivindicación 10 en donde la concentración de heptamolibdato de amonio es cerca de 2,5 por ciento.
15. La composición de la reivindicación 10 comprende cerca de 2,5 por ciento de cloruro de amonio y cerca de 2,5 por ciento de heptamolibdato de amonio.
16. Un sustrato metálico que comprende:

Un sustrato de metal que contiene una superficie exterior, en donde dicho metal se selecciona del grupo que consiste de Zinc, magnesio, aluminio, manganeso, y aleaciones y mezclas intermetálicas de estos; y

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Un recubrimiento de oscurecimiento dispuesto en dicho sustrato, dicho recubrimiento formado de una composición acuosa que comprende (i) de cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio, y (ii) de cerca de 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio, en donde la proporción de cloruro de amonio para el molibdato de amonio es de cerca de 1:3 a cerca de 3:1.

17. El sustrato recubierto de la reivindicación 16 que comprende además:

Un recubrimiento resistente a la corrosión dispuesto en dicho recubrimiento de oscurecimiento en donde dicho recubrimiento resistente a la corrosión comprende láminas de Zinc y láminas de aluminio dispersas en un ligador inorgánico.

18. El sustrato recubierto de la reivindicación 16 en donde dicha proporción es de cerca de 1:2 a cerca de 2:1.

19. El sustrato recubierto de la reivindicación 16 en donde dicha proporción es de cerca de 1:1.

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20. El sustrato recubierto de la reivindicación 16 en donde la concentración de cloruro de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.
21. El sustrato recubierto de la reivindicación 16 en donde la concentración de cloruro de amonio es de cerca de 2,5 por ciento.
22. El sustrato recubierto de la reivindicación 16 en donde la concentración de molibdato de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.
23. El sustrato recubierto de la reivindicación 16 en donde la concentración de molibdato de amonio es de cerca de 2,5 por ciento.
24. El sustrato recubierto de la reivindicación 16 en donde la concentración de cloruro de amonio es de cerca de 2,5 por ciento y la concentración de molibdato de amonio es de 2,5 por ciento.
25. El sustrato recubierto de la reivindicación 16 que comprende además:

Un recubrimiento resistente a la corrosión dispuesto en dicho recubrimiento de oscurecimiento en donde dicho recubrimiento resistente a la corrosión comprende láminas

de Zinc y láminas de aluminio dispersas en un ligador orgánico.

26. Un método para oscurecimiento de la superficie de Zinc comprende:

Suministrar un sustrato que tiene una superficie exterior de Zinc;

Suministrar una composición que incluye cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio y cerca de 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio; y

Aplicar dicha composición a dicha superficie exterior de dicho Zinc para formar un recubrimiento de oscurecimiento en esta.

27. El método de la reivindicación 26 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Secar dicho recubrimiento en una temperatura de cerca de 37 °C (100°F) a cerca de 121°C (250°F).

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28. El método de la reivindicación 26 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Exponer dicho recubrimiento a una operación de curado.

29. El método de la reivindicación 26 en donde dicha composición comprende de cerca de 0,5 por ciento a cerca de 3 por ciento de cloruro de amonio y cerca de 0,5 por ciento a 3 por ciento de molibdato de amonio.

30. El método de la reivindicación 26 en donde dicha composición comprende de cerca de 2,5 por ciento de cloruro de amonio y cerca de 2,5 por ciento de molibdato de amonio.

31. Un método para impartir corrosión que inhibe propiedades a un sustrato de un metal activo, dicho método comprende:

Suministrar un sustrato de un metal activo;

Suministrar una composición que incluye de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio y cerca 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio, en donde la proporción de cloruro de amonio a molibdato de amonio es de 1:3 a cerca de 3:1; y

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Aplicando dicha composición de dicho sustrato.

32. El método de la reivindicación 31 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Secar dicho recubrimiento en una temperatura de cerca de 37 °C (100°F) a cerca de 121°C (250°F).

33. El método de la reivindicación 31 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Exponer dicho recubrimiento a una operación de curado.

34. El método de la reivindicación 31 en donde dicha composición comprende de cerca de 0,5 por ciento a cerca de 3 por ciento de cloruro de amonio y cerca de 0,5 por ciento a 3 por ciento de molibdato de amonio.

35. El método de la reivindicación 31 en donde dicha composición comprende de cerca de 2,5 por ciento de cloruro de amonio y cerca de 2,5 por ciento de molibdato de amonio.

36. Un método para impartir propiedades de resistencia a la corrosión para una superficie de Zinc, dicho método comprende:

Suministrar un componente que tiene una superficie exterior de Zinc;

Suministrar una composición que incluye de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio y cerca 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio;
y

Aplicar dicha composición a dicha superficie exterior de dicho Zinc.

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#6REIVINDICACIONES

[Recibido por la Oficina Internacional el 10 de Diciembre del
2004 (10.12.2004): reivindicaciones originales 1-36
reemplazadas por las reivindicaciones corregidas 1-36 (5
páginas)]

Reivindicamos:

1. Una composición adaptada para oscurecer e impartir propiedades resistentes a la corrosión para una superficie metálica seleccionada de zinc, magnesio, manganeso, y aleaciones y mezclas intermetálicas de estos, la composición consiste esencialmente de:

De cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio;

De cerca de 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio;

Y

Cerca de 90 por ciento a cerca de 99,8 por ciento de agua;
en donde la proporción de cloruro de amonio para el molibdato de amonio es cerca de 1:2 a 2:1.

2. (cancelada)

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3. La composición de la reivindicación 1 en donde dicha proporción es de 1:1.
4. La composición de la reivindicación 1 en donde la concentración de cloruro de amonio es de 0,5 por ciento a cerca de 3 por ciento
5. La composición de la reivindicación 1 en donde la concentración de cloruro de amonio es de cerca de 2,5 por ciento
6. La composición de la reivindicación 1 en donde la concentración de molibdato de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.
7. La composición de la reivindicación 1 en donde la concentración de molibdato de amonio es cerca de 2,5 por ciento.
8. Una composición acuosa adaptada para aplicación a una superficie metálica seleccionada de zinc, magnesio, manganeso y aleaciones y mezclas intermetálicas de estos, la composición comprende:

De cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio; y de cerca de 0,1 por ciento a cerca de 5 por ciento de heptamolibdato de amonio;

En donde la proporción de cloruro de amonio para el heptamolibdato de amonio es cerca de 1:3 a cerca de 3:1.

9. La composición de la reivindicación 8 en donde dicha proporción es de 1:2 a cerca de 2:1.
10. La composición de la reivindicación 8 en donde dicha proporción es de 1:1
11. La composición de la reivindicación 8 en donde la concentración de cloruro de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.
12. La composición de la reivindicación 10 en donde la concentración de cloruro de amonio es de cerca de 2,5 por ciento.
13. La composición de la reivindicación 8 en donde la concentración de heptamolibdato de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.
14. La composición de la reivindicación 10 en donde la concentración de heptamolibdato de amonio es cerca de 2,5 por ciento.

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15. La composición de la reivindicación 10 comprende cerca de 2,5 por ciento de cloruro de amonio y cerca de 2,5 por ciento de heptamolibdato de amonio.

16. Un sustrato metálico recubierto que comprende:

Un sustrato de metal que contiene una superficie exterior, en donde dicho metal se selecciona del grupo que consiste de Zinc, magnesio, aluminio, manganeso, y aleaciones y mezclas intermetálicas de estos; y

Un recubrimiento de oscurecimiento dispuesto en dicho sustrato, dicho recubrimiento formado de una composición acuosa que comprende esencialmente (i) de cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio, y (ii) de cerca de 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio, en donde la proporción de cloruro de amonio para el molibdato de amonio es de cerca de 1:2 a cerca de 2:1.

17. El sustrato recubierto de la reivindicación 16 que comprende además:

Un recubrimiento resistente a la corrosión dispuesto en dicho recubrimiento de oscurecimiento en donde dicho

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recubrimiento resistente a la corrosión comprende láminas de Zinc y láminas de aluminio dispersas en un ligador inorgánico.

18. (cancelada).

19. El sustrato recubierto de la reivindicación 16 en donde dicha proporción es de cerca de 1:1.

20. El sustrato recubierto de la reivindicación 16 en donde la concentración de cloruro de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.

21. El sustrato recubierto de la reivindicación 16 en donde la concentración de cloruro de amonio es de cerca de 2,5 por ciento.

22. El sustrato recubierto de la reivindicación 16 en donde la concentración de molibdato de amonio es de cerca de 0,5 por ciento a cerca de 3 por ciento.

23. El sustrato recubierto de la reivindicación 16 en donde la concentración de molibdato de amonio es de cerca de 2,5 por ciento.

24. El sustrato recubierto de la reivindicación 16 en donde la concentración de cloruro de amonio es de

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not

cerca de 2,5 por ciento y la concentración de molibdato de amonio es de 2,5 por ciento.

25. El sustrato recubierto de la reivindicación 16 que comprende además:

Un recubrimiento resistente a la corrosión dispuesto en dicha superficie exterior de dicho sustrato de metal y dicho recubrimiento de oscurecimiento, en donde dicho recubrimiento resistente a la corrosión comprende láminas de Zinc y láminas de aluminio dispersas en un ligador orgánico.

26. Un método para oscurecimiento de la superficie de Zinc comprende:

Suministrar un sustrato que tiene una superficie exterior de Zinc;

Suministrar una composición que incluye cerca de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio y cerca de 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio; y

Aplicar dicha composición a dicha superficie exterior de dicho Zinc para formar un recubrimiento de oscurecimiento en esta.

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27. El método de la reivindicación 26 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Secar dicho recubrimiento en una temperatura de cerca de 37 °C (100°F) a cerca de 121°C (250°F).

28. El método de la reivindicación 26 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Exponer dicho recubrimiento a una operación de curado.

29. El método de la reivindicación 26 en donde dicha composición comprende de cerca de 0,5 por ciento a cerca de 3 por ciento de cloruro de amonio y cerca de 0,5 por ciento a 3 por ciento de molibdato de amonio.

30. El método de la reivindicación 26 en donde dicha composición comprende de cerca de 2,5 por ciento de cloruro de amonio y cerca de 2,5 por ciento de molibdato de amonio.

31. Un método para impartir corrosión que inhibe propiedades a un sustrato de un metal activo, dicho método comprende:

Suministrar un sustrato de un metal activo;

Suministrar una composición que incluye de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio y cerca 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio, en donde la proporción de cloruro de amonio a molibdato de amonio es de 1:3 a cerca de 3:1; y

Aplicando dicha composición de dicho sustrato.

32. El método de la reivindicación 31 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Secar dicho recubrimiento en una temperatura de cerca de 37 °C (100°F) a cerca de 121°C (250°F).

33. El método de la reivindicación 31 que comprende además, después de dicha etapa de aplicar dicha composición, una etapa de:

Exponer dicho recubrimiento a una operación de curado.

34. El método de la reivindicación 31 en donde dicha composición comprende de cerca de 0,5 por ciento a cerca de 3 por ciento de cloruro de amonio y cerca de 0,5 por ciento a 3 por ciento de molibdato de amonio.

35. El método de la reivindicación 31 en donde dicha composición comprende de cerca de 2,5 por ciento de cloruro de amonio y cerca de 2,5 por ciento de molibdato de amonio.

36. Un método para impartir propiedades de resistencia a la corrosión para una superficie de Zinc, dicho método comprende:

Suministrar un componente que tiene una superficie exterior de Zinc;

Suministrar una composición que incluye de 0,1 por ciento a cerca de 5 por ciento de cloruro de amonio y cerca 0,1 por ciento a cerca de 5 por ciento de molibdato de amonio; y

Aplicar dicha composición a dicha superficie exterior de dicho Zinc.

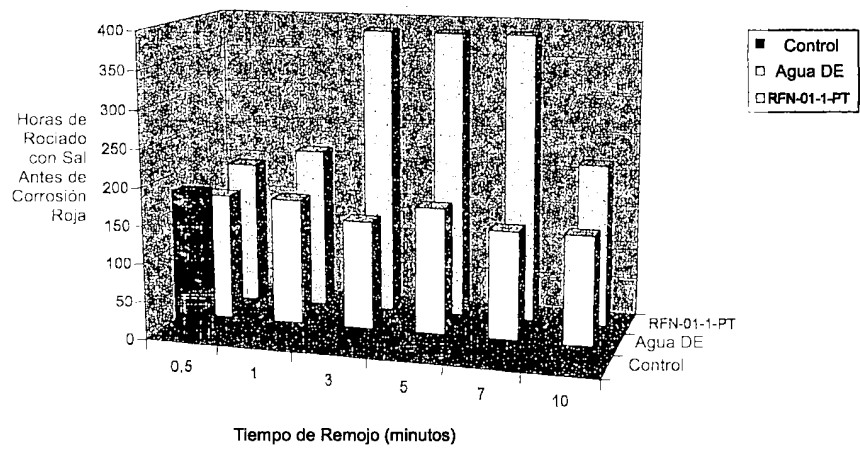
COMPARACIONES Y MÉTODOS PARA OSCURECER IMPARTIR PROPIEDADES
DE RESISTENCIA A LA CORROSIÓN AL ZINC U OTROS METALES ACTIVOS

4

Resumen

Se describen métodos y composiciones que sirven para oscurecer zinc u otra superficie de metal activa e impartir propiedades de de la corrosión a ésta Las composiciones incluyen una solución acuosa que contiene aproximadamente 0.1% aproximadamente 5% de cloruro de amonio y aproximadamente 0.1% aproximadamente 5% de anhídrido de amonio. De las composiciones utilizan proporciones particulares de concentraciones de cloruro de amonio y anhídrido de amonio.

Figura 1.
Baño a Temperatura Ambiente/Secado al Aire



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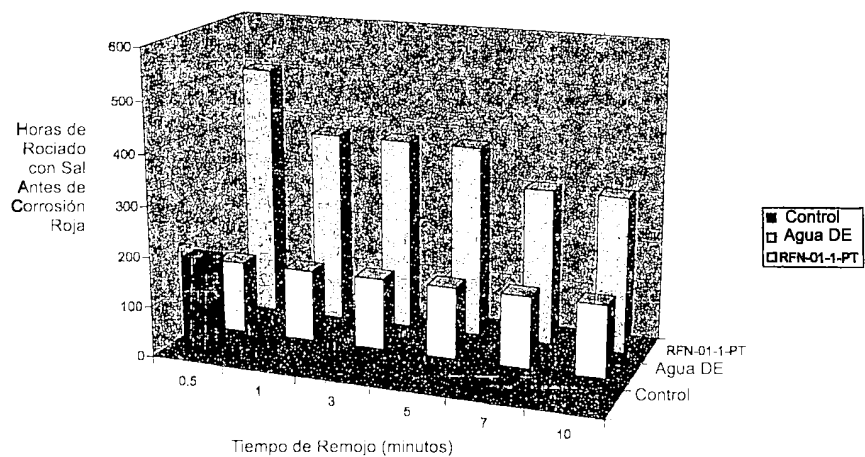
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Figura 2.
Baño a 150° F /Secado al Aire



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Figura3.
Baño a temperatura Ambiente/ Secado 350° F

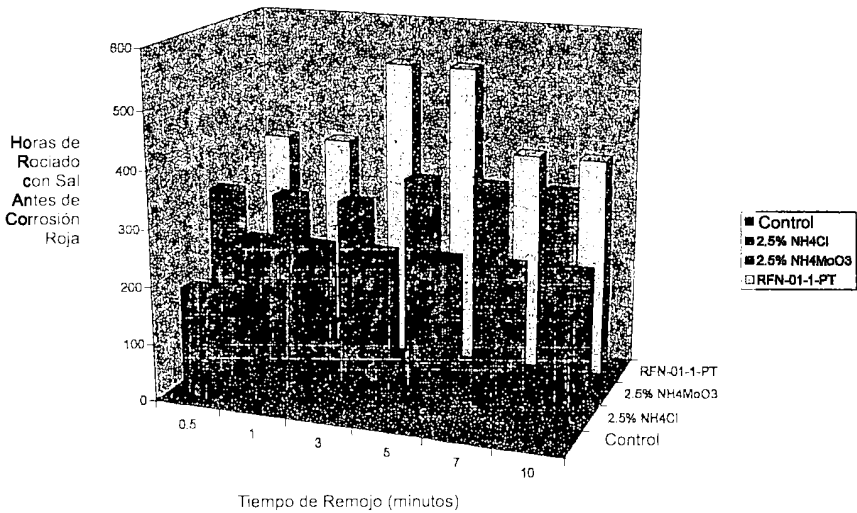
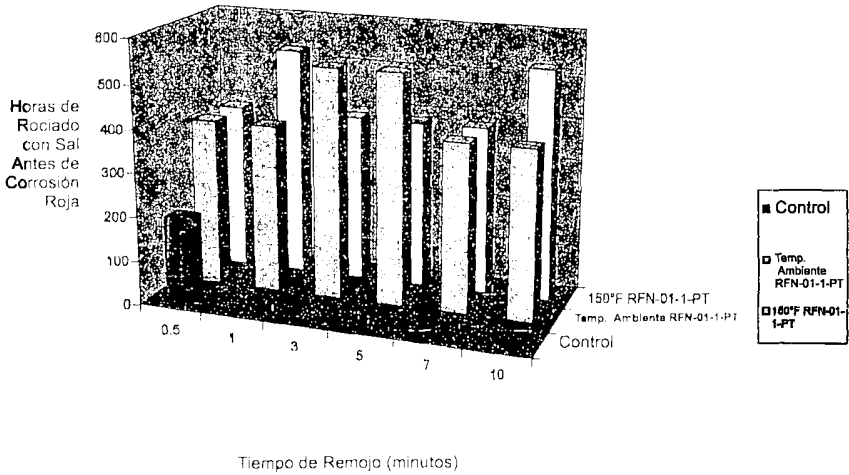


Figura 4.
RFN-01-1-PT Horneado a 350° F



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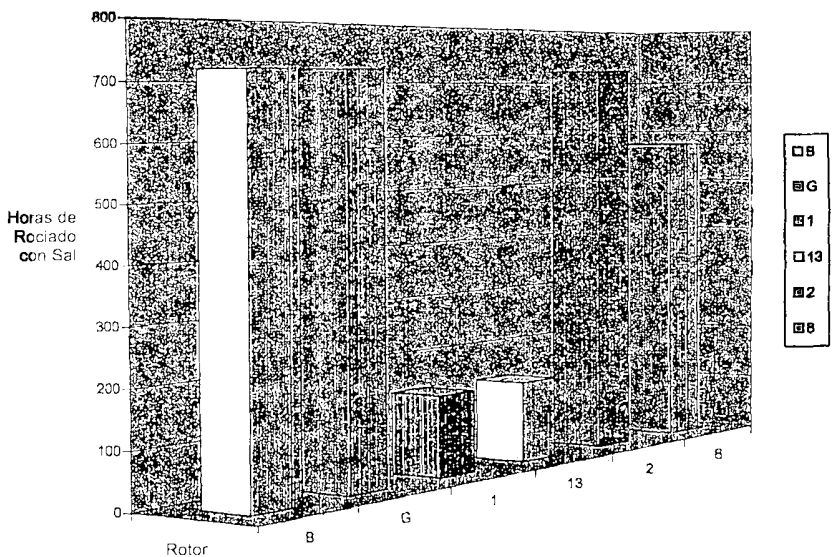
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Figura 6.
Primera Corrosión Roja



PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

RECEIVED

MAR 17 2005

FAY, SHARPE, FAGAN,
MINNICH & MCKEE, LLP

To:
MARK E. BANDY
FAY, SHARPE, FAGAN, MINNICH & MCKEE, LLP
1100 SUPERIOR AVENUE, SUITE 700
CLEVELAND, OH 44114

PCT

NOTIFICATION OF TRANSMITTAL OF
INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)

(PCT Rule 71.1)

Date of mailing
(day/month/year)

14 MAR 2005

Applicant's or agent's file reference

MCII20002PCT

IMPORTANT NOTIFICATION

International application No.

International filing date (day/month/year)

Priority date (day/month/year)

PCT/US04/17786

04 June 2004 (04.06.2004)

05 June 2003 (05.06.2003)

Applicant

METAL COATINGS INTERNATIONAL INC.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the *PCT Applicant's Guide*.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed invention is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the IPEA/ US

Mail Stop PCT, Attn: IPEA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Matthew A. Thexton

Telephone No. 571-272-1125

Form PCT/IPEA/416 (January 2004)

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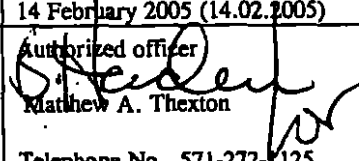
PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference MCII20002PCT	FOR FURTHER ACTION		See Form PCT/IPEA/416
International application No. PCT/US04/17786	International filing date (day/month/year) 04 June 2004 (04.06.2004)	Priority date (day/month/year) 05 June 2003 (05.06.2003)	
International Patent Classification (IPC) or national classification and IPC IPC(7): B32B 15/04; C23C 22/40, 68, 82; C23F 11/00; C09K 13/04 and US Cl.: See Electronic data bases.			
Applicant METAL COATINGS INTERNATIONAL INC.			
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of <u>5</u> sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. ☒ (sent to the applicant and to the International Bureau) a total of <u>5</u> sheets, as follows: ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box. b. ☐ (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) _____, containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).			
4. This report contains indications relating to the following items: ☒ Box No. I Basis of the report ☐ Box No. II Priority ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability ☒ Box No. IV Lack of unity of invention ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement ☐ Box No. VI Certain documents cited ☐ Box No. VII Certain defects in the international application ☒ Box No. VIII Certain observations on the international application			
Date of submission of the demand 04 January 2005 (04.01.2005)		Date of completion of this report 14 February 2005 (14.02.2005)	
Name and mailing address of the IPEA/ US Mail Stop PCT, Attn: IPEA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230		Authorized officer  Matthew A. Thexton Telephone No. 571-272-1125	

Form PCT/IPEA/409 (cover sheet)(January 2004)

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/US04/17786

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Box No. I Basis of the report

1. With regard to the language, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on translations from the original language into the following language _____, which is the language of a translation furnished for the purposes of:

- ☐ international search (under Rules 12.3 and 23.1(b))
☐ publication of the international application (under Rule 12.4)
☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

☐ the international application as originally filed/furnished

☒ the description:

pages 1-24 as originally filed/furnished

pages* NONE received by this Authority on _____

pages* NONE received by this Authority on _____

☒ the claims:

pages NONE as originally filed/furnished

pages* NONE as amended (together with any statement) under Article 19

pages* 25-29 received by this Authority on 04 January 2005 (04.01.2005)

pages* NONE received by this Authority on _____

☒ the drawings:

pages 1-6 as originally filed/furnished

pages* NONE received by this Authority on _____

pages* NONE received by this Authority on _____

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:

☐ the description, pages _____

☒ the claims, Nos. 2, 18

☐ the drawings, sheets/figs _____

☐ the sequence listing (specify): _____

☐ any table(s) related to the sequence listing (specify): _____

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

☐ the description, pages _____

☐ the claims, Nos. _____

☐ the drawings, sheets/figs _____

☐ the sequence listing (specify): _____

☐ any table(s) related to the sequence listing (specify): _____

* If item 4 applies, some or all of those sheets may be marked "superseded."

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✓

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/US04/17786

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application
☒ claims Nos. 26-36

because:

- ☐ the said international application, or the said claim Nos. _____ relate to the following subject matter which does not require an international preliminary examination (*specify*):

- ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. _____ are so unclear that no meaningful opinion could be formed (*specify*):

- ☐ the claims, or said claims Nos. _____ are so inadequately supported by the description that no meaningful opinion could be formed.

- ☒ no international search report has been established for said claims Nos. 26-36

- ☐ the nucleotide and/or amino acid sequence listing does not comply with the standard provided for in Annex C of the Administrative Instructions in that:

the written form

☐

has not been furnished

☐

does not comply with the standard

the computer readable form

☐

has not been furnished

☐

does not comply with the standard

- ☐ the tables related to the nucleotide and/or amino acid sequence listing, if in computer readable form only, do not comply with the technical requirements provided for in Annex C-*bis* of the Administrative Instructions.

- ☐ See Supplemental Box for further details.

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/US04/17786

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Box No. IV Lack of unity of invention

1. ☒ In response to the invitation to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.
☒ paid additional fees.
☐ paid additional fees under protest.
☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is:

- ☐ complied with.
☒ not complied with for the following reasons:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1 and 3-15, drawn to formulations comprising aqueous solutions of ammonium chloride and ammonium molybdate/heptamolybdate.

Group II, claim(s) 16, 17, and 19-25, drawn to metallic substrates treated with the formulations of claims 1 and 3-15.

Group III, claim(s) 26-36, drawn to methods of treating metallic substrates with the formulations of claims 1 and 3-15.

The inventions listed as Groups I, II, and III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The common technical features to all claims are found in the formulation of claim 1. This formulation is known as disclosed by Lewis et al. (US 2554526), see column 1, lines 50 to column 2, line 3; accordingly, such does not constitute an advancement in the art and is not a "special" technical features as required for unity of invention.

4. Consequently, this report has been established in respect of the following parts of the international application:

- ☐ all parts
☒ the parts relating to claims Nos. 1,2-17,19-25

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US04/17786

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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims <u>8-15,17,25</u>	YES
	Claims <u>1,3-7,16,19-24</u>	NO
Inventive Step (IS)	Claims <u>17</u>	YES
	Claims <u>1, 3-7, 16, 19-25</u>	NO
Industrial Applicability (IA)	Claims <u>1,3-17,19-25</u>	YES
	Claims <u>NONE</u>	NO

2. Citations and Explanations (Rule 70.7)
Please See Continuation Sheet

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/US04/17786

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Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 1, 3-17, and 19-25 are objected to as lacking clarity under PCT Rule 66.2(a)(v) because of the claims being not fully supported by the description. The description does not disclose the claimed invention in a manner sufficiently clear and complete for the claimed invention to be carried out by a person skilled in the art because: *The formulations are not described as to the basis upon which they are to be created; i.e., weight percent, volume percent, mol percent, or otherwise.*

Claims 1, 3-17, and 19-25 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because claims 1,3-17,19-25 are indefinite for the following reason(s): *The claimed formulations are not specified as to the basis upon which they are to be created; i.e., weight percent, volume percent, mol percent, or otherwise.*

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Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of:

V. 2. Citations and Explanations:

Claims 1, and 3-7 lack novelty under PCT Article 33(2) as being anticipated by Shipley, Jr., et al. (US 3650957). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate (column 4, line 74 to column 5, line 65; examples 12, 13, and 19). Concentrations are "about" 1:1 (claims 8-10) and 2.5 percent, as required by the claims.

Claims 1, 3-7, 16, and 19-24 lack novelty under PCT Article 33(2) as being anticipated by Mitchell et al. (US 3314811). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate at "about" 1:1 by weight (column 3, lines 8-18), concentration determined at "about 1 ounce to about 3 pounds" per gallon of water (there are 8.34 pounds per gallon of water) (see claim 1) is "about" 2.5 percent, as required by claims 1-7. Such are for blackening aluminum substrates. Coated substrates with corrosion resistance are disclosed, as required by claims 16 and 18-24.

Claims 1, 3-7, 16, and 19-24 lack novelty under PCT Article 33(2) as being anticipated by Lewis et al. (US 2554256). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate at "about" 1:1 by weight and concentration of "about" 2.5 percent (column 4, lines 15-18), as required by the claims. Such are for coloring aluminum substrates. Coated aluminum substrates with corrosion resistance are disclosed (column 3, lines 52-55), as required by claims 16 and 18-24.

Claims 1, 3-7, 16, and 19-24 lack novelty under PCT Article 33(2) as being anticipated by Belkin et al. (SU 1678900 A1, as evidenced by USPTO obtained translation). The reference discloses aqueous formulations of ammonium chloride and ammonium molybdate at "about" 1:1 and "about" 2.5 percent, as required by claims 1-7. Aluminum substrates are coated to provide corrosion protection, as required by claims 16 and 18-24.

Claims 1, 3-7, 16, and 19-24 lack novelty under PCT Article 33(2) as being anticipated by Merekina et al. (SU 827613 B, as evidenced by USPTO obtained translation). The reference discloses aqueous formulations of ammonium chloride and ammonium molybdate at "about" 1:1 and "about" 2.5 percent, as required by claims 1-7. Zinc substrates are coated to provide corrosion protection, as required by claims 16 and 18-24.

Claims 8-15 lack an inventive step under PCT Article 33(3) as being obvious over Shipley, Jr., et al. (US 3650957). The reference discloses that the source of the complexing molybdenum compound is not critical (column 5, lines 15-18). Thus, it would have been obvious to the ordinary artisan to employ any commercially available molybdate, such as heptamolybdate.

Claims 8-15 and 25 lack an inventive step under PCT Article 33(3) as being obvious over Mitchell et al. (US 3314811) in view of

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Supplemental Box

Paulet (US 4018628). The Paulet reference is directed to formulations for blackening aluminum, as is the Mitchell reference. The Paulet reference discloses ammonium molybdate or heptamolybdate (column 2, lines 4-7). It would have been obvious to the ordinary artisan to modify the formulations of the Mitchell reference in view of the disclosure of equivalence in the Paulet reference for reasons of economics or availability. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosures of the references for blackening/coloring.

Claims 8-15 and 25 lack an inventive step under PCT Article 33(3) as being obvious over Lewis et al. (US 2554256) in view of Paulet (US 4018628). The Paulet reference is directed to formulations for blackening aluminum, as is the Lewis reference. The Paulet reference discloses ammonium molybdate or heptamolybdate (column 2, lines 4-7). It would have been obvious to the ordinary artisan to modify the formulations of the Lewis reference in view of the disclosure of equivalence in the Paulet reference for reasons of economics or availability. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosures of the references for blackening/coloring.

Claim 25 lacks an inventive step under PCT Article 33(3) as being obvious over Belkin et al. (SU 1678900 A1, as evidenced by USPTO obtained translation). Aluminum substrates are coated to provide corrosion protection, as required by claim 25. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosure of the reference for coating.

Claim 25 lacks an inventive step under PCT Article 33(3) as being obvious over Merekina et al. (SU 827613 B, as evidenced by USPTO obtained translation). Zinc substrates are coated to provide corrosion protection, as required by claim 25. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosure of the reference for coating.

Claims 1, 3-17, and 19-25 satisfy the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

Claim 17 satisfies the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest further providing upon the coated substrates resulting from coating the zinc or aluminum substrate with the respective formulations a corrosion resistant coating of zinc and aluminum flakes in an inorganic binder.

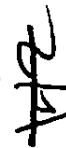
Applicant's amendments to claims 1 and 16 are noted. Applicant's Remarks are noted. In response it is noted that Applicant has not provided any indication of original support in the Application for the contention that the percentages in the claims and specification are expressed in weight percent; the artisan would have to experiment to determine the metes and bounds of the invention. In response it is noted that Applicant has not provided any facts or reasoning to support the contention that any of the references' compositions contain ingredients that would materially affect the basic and novel characteristics of the claimed invention. In response it is noted that the metallic surface may be an alloy, which encompasses aluminum alloys having one or more of the recited metals.

NEW CITATIONS

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We claim:

1. A composition adapted for darkening and imparting corrosion-resistant properties to a metallic surface selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, the composition
5 consisting essentially of:
from about 0.1 percent to about 5 percent ammonium chloride;
from about 0.1 percent to about 5 percent ammonium molybdate;
and
from about 90 percent to about 99.8 percent water;
10 wherein the ratio of ammonium chloride to ammonium molybdate is
from about 1:2 to about 2:1.
2. (Canceled)
- 15 3. The composition of claim 1 wherein said ratio is about 1:1.
4. The composition of claim 1 wherein the concentration of ammonium chloride is from about 0.5 percent to about 3 percent.
- 20 5. The composition of claim 1 wherein the concentration of ammonium chloride is about 2.5 percent.
6. The composition of claim 1 wherein the concentration of ammonium molybdate is from about 0.5 percent to about 3 percent.
- 25 7. The composition of claim 1 wherein the concentration of ammonium molybdate is about 2.5 percent.
8. An aqueous composition adapted for application to a metallic
30 surface selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, the composition comprising:
from about 0.1 percent to about 5 percent ammonium chloride; and

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from about 0.1 percent to about 5 percent ammonium heptamolybdate;

wherein the ratio of ammonium chloride to ammonium heptamolybdate is from about 1:3 to about 3:1.

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9. The composition of claim 8 wherein said ratio is from about 1:2 to about 2:1.

10. The composition of claim 8 wherein said ratio is about 1:1.

10

11. The composition of claim 8 wherein the concentration of ammonium chloride is from about 0.5 percent to about 3 percent.

12. The composition of claim 10 wherein the concentration of ammonium chloride is about 2.5 percent.

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13. The composition of claim 8 wherein the concentration of ammonium heptamolybdate is from about 0.5 percent to about 3 percent.

14. The composition of claim 10 wherein the concentration of ammonium heptamolybdate is about 2.5 percent.

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15. The composition of claim 10 comprising about 2.5 percent ammonium chloride and about 2.5 percent ammonium heptamolybdate.

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16. A coated metallic substrate comprising:

a metal substrate having an outer surface, wherein said metal is selected from the group consisting of zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof; and

a darkening coating disposed on said substrate, said coating formed from an aqueous composition consisting essentially of (i) from about 0.1 percent to about 5 percent ammonium chloride, and (ii) from about 0.1 percent to

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about 5 percent ammonium molybdate, wherein the ratio of ammonium chloride to ammonium molybdate is from about 1:2 to about 2:1.

17. The coated substrate of claim 16 further comprising:
5 a corrosion-resistant coating disposed on said darkening coating, wherein said corrosion-resistant coating comprises zinc flakes and aluminum flakes dispersed in an inorganic binder.
18. (Canceled)
19. The coated substrate of claim 16 wherein said ratio is about 1:1.
20. The coated substrate of claim 16 wherein the concentration of ammonium chloride is from about 0.5 percent to about 3 percent.
21. The coated substrate of claim 16 wherein the concentration of ammonium chloride is about 2.5 percent.
22. The coated substrate of claim 16 wherein the concentration of ammonium molybdate is from about 0.5 percent to about 3 percent.
23. The coated substrate of claim 16 wherein the concentration of ammonium molybdate is about 2.5 percent.
24. The coated substrate of claim 16 wherein the concentration of ammonium chloride is about 2.5 percent and the concentration of ammonium molybdate is about 2.5 percent.
25. The coated substrate of claim 16 further comprising;
30 a corrosion-resistant coating disposed between said outer surface of said metal substrate and said darkening coating, wherein said corrosion-resistant coating comprises zinc flakes and aluminum flakes dispersed in an organic binder.

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26. A method for darkening the surface of zinc comprising:
providing a substrate having an outer surface of zinc;
providing a composition including from about 0.1 percent to about 5
5 percent ammonium chloride and from about 0.1 percent to about 5 percent
ammonium molybdate; and
applying said composition to said outer surface of said zinc to form
a darkening coating thereon.
- 10 27. The method of claim 26 further comprising, after said step of
applying said composition, a step of:
drying said coating at a temperature of from about 37°C (100°F) to
about 121°C (250°F).
- 15 28. The method of claim 26 further comprising, after said step of
applying said composition, a step of:
exposing said coating to a curing operation.
- 20 29. The method of claim 26 wherein said composition comprises from
about 0.5 percent to about 3 percent ammonium chloride and from about 0.5
percent to about 3 percent ammonium molybdate.
- 30 30. The method of claim 26 wherein said composition comprises about
2.5 percent ammonium chloride and about 2.5 percent ammonium molybdate.
- 25 31. A method for imparting corrosion inhibiting properties to a substrate
of an active metal, said method comprising:
providing a substrate of an active metal;
providing a composition including from about 0.1 percent to about 5
30 percent ammonium chloride and from about 0.1 percent to about 5 percent
ammonium molybdate, wherein the ratio of ammonium chloride to ammonium
molybdate is from about 1:3 to about 3:1; and
applying said composition to said substrate.

32. The method of claim 31 further comprising, after said step of
applying said composition, a step of:
drying said coating at a temperature of from about 37°C (100°F) to
5 about 121°C (250°F).

33. The method of claim 31 further comprising, after said step of
applying said composition, a step of:
10 exposing said coating to a curing operation.

34. The method of claim 31 wherein said composition comprises from
about 0.5 percent to about 3 percent ammonium chloride and from about 0.5
percent to about 3 percent ammonium molybdate.

15 35. The method of claim 31 wherein said composition comprises about
2.5 percent ammonium chloride and about 2.5 percent ammonium molybdate.

36. A method for imparting corrosion resistance properties to a zinc
surface, said method comprising:
20 providing a component having an outer surface of zinc;
providing a composition including from about 0.1 percent to about 5
percent ammonium chloride and from about 0.1 percent to about 5 percent
ammonium molybdate; and
applying said composition to said outer surface of said zinc.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference MCII20002PCT	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/US04/17786	International filing date (day/month/year) 04 June 2004 (04.06.2004)	(Earliest) Priority Date (day/month/year) 05 June 2003 (05.06.2003)
Applicant PEARCE ET AL.		

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

This international search report consists of a total of 5 sheets.



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

1. Basis of the Report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).



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

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

3. ☒ Unity of invention is lacking (See Box No. III)

4. With regard to the title,



the text is approved as submitted by the applicant.



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

5. With regard to the abstract,



the text is approved as submitted by the applicant.



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

6. With regard to the drawings,

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



as suggested by the applicant.



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



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



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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/17786

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-6/21

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.: 1-25
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/17786

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B32B 15/04;C23C 22/40,68,82;C23F 11/00;C09K 13/04

US CL : See Electronic data bases.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : See Electronic data bases.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4798683 (BOFFARDI et al.) 17 January 1989 (17.01.1989), cited in application to show state of the art.	8-15
A	US 4548787 (WILSON et al.) 22 October 1985 (22.10.1985), cited in application to show the state of the art.	
A	US 4440721 (WILSON et al.) 3 April 1984 (03.04.1984), cited in application to show the state of the art.	
A	US 4409121 (LATOS et al.) 11 October 1983 (11.10.1983), cited in application to show the state of the art.	
A	US 4217216 (LIPINSKI, Richard J.) 12 August 1980 (12.08.1980), cited in application to show the state of the art.	
A	US 4176059 (SUZUKI, Fumiko) 27 November 1979 (27.11.1979), cited in application to show the state of the art.	
Y	US 4018628 (PAULET, Jean Francois) 19 April 1977 (19.04.1977), column 2, line 4-7; claim 1.	
A	US 3920488 (PITTON, Oscar) 18 November 1975 (18.11.1985), cited to show the state of the art.	



Further documents are listed in the continuation of Box C.



See patent family annex.

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

Date of the actual completion of the international search

03 September 2004 (03.09.2004)

Date of mailing of the international search report

13 OCT 2004

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Matthew A. Thexton

Telephone No. 571-272-1125

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US04/17786

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C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 3650957 (SHIPLEY, JR. et al.) 21 March 1972 (21.03.1972), examples 12, 13, 19; column 4, lines 55-57; column 5, lines 70-73.	1-7 8-15
X — Y	US 3314811 (MITCHELL et al.) 18 April 1967 (18.04.1967), column 2, lines 4-21; column 3, lines 48-57; claim 1.	1-7,16,18-24 8-15,25
X — Y	US 2554256 (LEWIS et al.) 22 May 1951 (22.05.1951), column 1, line 50 to column 2, line 3, column 3, lines 52-55.	1-7,16,18-24 8-15,25
X — Y	SU 1678900 A1, (BELKIN et al.) 23 September 1991 (23.09.1991).	1-7,16,18-24 25
X — Y	SU 1678900 A1, (BELKIN et al.) 23 September 1991 (23.09.1991), USPTO obtained translation, see abstract.	1-7,16,18-24 25
X — Y	SU 827613B, (MEREKINA et al.) 7 May 1981 (07.05.1981), USPTO obtained translation, see abstract.	1-7,16,18-24 25
X — Y	SU 827613B, (MEREKINA et al.) 7 May 1981 (07.05.1981).	1-7,16,18-24 25
A	LIENARD et al., "Analysis of the Mechanism of Selective Coloration Facilitating the Identification of Various Phases in Aluminum-Silicon-Copper Casting Alloys" <i>Homes Et Fonderie</i> , June-July, 1982, pp. 27-35, cited in application to show the state of the art.	
A	LIENARD et al., <i>ibid.</i> English language translation.	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US04/17786

15050

BOX III. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-15, drawn to formulations comprising aqueous solutions of ammonium chloride and ammonium molybdate/heptamolybdate.

Group II, claim(s) 16-25, drawn to metallic substrates treated with the formulations of claims 1-15.

Group III, claim(s) 26-36, drawn to methods of treating metallic substrates with the formulations of claims 1-15.

The inventions listed as Groups I, II, and III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The common technical features to all claims are found in claim 1. This formulation is known as disclosed by Lewis et al. (US 2554526), see column 1, line 50 to column 2, line 3, accordingly, such does not constitute an advancement in the art and is not a "special" technical feature as required for unity of invention.

Continuation of B. FIELDS SEARCHED Item 3:

In each instance, plurals automatically searched.

EAST: (252/79.1, 79.2 148/273, 272 106/14.21) and (molybdate molybdenum \$molybdate) and ammonium and chloride.

EAST: (428/472.1) and (molybdate molybdenum \$molybdate).

EPO, JPO, DERWENT, IBM-TDB: (coat coating layer coated) and (molybdate molybdenum \$molybdate) and ammonium and chloride.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/17786

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B32B 15/04;C23C 22/40,68,82;C23F 11/00;C09K 13/04
US CL : See Electronic data bases.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : See Electronic data bases.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4409121 (LATOS et al.) 11 October 1983 (11.10.1983), cited in application to show the state of the art.	
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A	US 4176059 (SUZUKI, Fumiko) 27 November 1979 (27.11.1979), cited in application to show the state of the art.	
Y	US 4018628 (PAULET, Jean Francois) 19 April 1977 (19.04.1977), column 2, line 4-7; claim 1.	
A	US 3920488 (PITTON, Oscar) 18 November 1975 (18.11.1985), cited to show the state of the art.	



Further documents are listed in the continuation of Box C.



See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
03 September 2004 (03.09.2004)	13 OCT 2004
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	Authorized officer Matthew A. Thexton Telephone No. 571-272-1125

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US04/17786

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 3650957 (SHIPLEY, JR. et al.) 21 March 1972 (21.03.1972), examples 12, 13, 19; column 4, lines 55-57; column 5, lines 70-73.	1-7 — 8-15
X — Y	US 3314811 (MITCHELL et al.) 18 April 1967 (18.04.1967), column 2, lines 4-21; column 3, lines 48-57; claim 1.	1-7,16,18-24 — 8-15,25
X — Y	US 2554256 (LEWIS et al.) 22 May 1951 (22.05.1951), column 1, line 50 to column 2, line 3, column 3, lines 52-55.	1-7,16,18-24 — 8-15,25
X — Y	SU 1678900 A1, (BELKIN et al.) 23 September 1991 (23.09.1991).	1-7,16,18-24 — 25
X — Y	SU 1678900 A1, (BELKIN et al.) 23 September 1991 (23.09.1991), USPTO obtained translation, see abstract.	1-7,16,18-24 — 25
X — Y	SU 827613B, (MEREKINA et al.) 7 May 1981 (07.05.1981), USPTO obtained translation, see abstract.	1-7,16,18-24 — 25
X — Y	SU 827613B, (MEREKINA et al.) 7 May 1981 (07.05.1981).	1-7,16,18-24 — 25
A	LIENARD et al., "Analysis of the Mechanism of Selective Coloration Facilitating the Identification of Variou Phases in Aluminum-Silicon-Copper Casting Alloys" <i>Homes Et Fonderie</i> , June-July, 1982, pp. 27-35, cited in application to show the state of the art.	
A	LIENARD et al., <i>ibid.</i> English language translation.	

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/17786

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5

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.: 1-25
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/17786

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BOX III. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-15, drawn to formulations comprising aqueous solutions of ammonium chloride and ammonium molybdate/heptamolybdate.

Group II, claim(s) 16-25, drawn to metallic substrates treated with the formulations of claims 1-15.

Group III, claim(s) 26-36, drawn to methods of treating metallic substrates with the formulations of claims 1-15.

The inventions listed as Groups I, II, and III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The common technical features to all claims are found in claim 1. This formulation is known as disclosed by Lewis et al. (US 2554526), see column 1, line 50 to column 2, line 3, accordingly, such does not constitute an advancement in the art and is not a "special" technical feature as required for unity of invention.

Continuation of B. FIELDS SEARCHED Item 3:

In each instance, plurals automatically searched.

EAST: (252/79.1,79.2 148/273,272 106/14.21) and (molybdate molybdenum \$molybdate) and ammonium and chloride.

EAST: (428/472.1) and (molybdate molybdenum \$molybdate).

EPO,JPO,DERWENT,IBM-TDB: (coat coating layer coated) and (molybdate molybdenum \$molybdate) and ammonium and chloride.

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

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

(PCT Rule 44.1)

To:
MARK E. BANDY
FAY, SHARPE, FAGAN, MINNICH & MCKEE, LLP
1100 SUPERIOR AVENUE, SUITE 700
CLEVELAND, OH 44114

Date of mailing
(day/month/year) **13 OCT 2004**

Applicant's or agent's file reference
MCII20002PCT

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.
PCT/US04/17786

International filing date
(day/month/year) 04 June 2004 (04.06.2004)

Applicant
METAL COATINGS INTERNATIONAL, INC.

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

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

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

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

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

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

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

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

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

4. **Reminders**

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

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

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

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

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

Name and mailing address of the ISA/ US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
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Facsimile No. (703) 305-3230

Authorized officer

RICHARD CRISPINO

Telephone No. 571 272-700

156 56

Spec.

Analyse du mecanisme de coloration selective facilitant l'identification de diverses phases dans les alliages de fonderie Aluminium-Silicium-Cuivre



Philippe LIENARD,
Ingénieur civil A.J.M.
Assistant



Professeur Clément PACQUÉ,
Ingénieur civil A.J.M.

Faculté Polytechnique de MONS (Belgique)

INTRODUCTION

L'utilisation du silicium comme élément d'addition de l'aluminium pour réaliser des pièces moulées est connue depuis longtemps. A côté de la gamme des ATB40 et des ALS10G, les fondeurs disposent depuis une dizaine d'années d'une série d'alliages contenant de 5 à 7 % de silicium qui permettent notamment d'obtenir sans difficultés des pièces étanches [1] [2] [3].

Outre cette caractéristique les AFS7 possèdent de bonnes propriétés de fonderie qui s'expliquent par la forme du diagramme d'équilibre «aluminium-silicium», c'est-à-dire :

- un écart liquide-solide faible,
- une proportion d'eutectique importante,
- une basse température de fusion,

La morphologie de la structure de solidification de l'eutectique aluminium-silicium a une influence prépondérante sur les propriétés mécaniques des alliages. Les alliages industriels aluminium-silicium hypoeutectiques contiennent essentiellement en plus de l'impureté phosphore (quelques p.p.m. à une dizaine) deux éléments : le fer, impureté provenant de l'aluminium d'électrolyse, et le magnésium, élément d'addition nécessaire à l'obtention de bonnes propriétés mécaniques. Leur effet structural lors de la solidification peut se résumer ainsi :

- 1) des additions de fer jusqu'à 1 % n'ont pas d'effet décelable sur l'eutectique, il reste lamellaire très fin
- 2) des teneurs en magnésium de 0,3 à 0,8 % environ lui donne toujours une forme aciculaire.

Un traitement de modification sur le métal liquide par des éléments tels le sodium, le strontium ou l'antimoine est alors nécessaire si l'on veut accroître les caractéristiques mécaniques de l'alliage par une répartition fine et dispersée des grains de silicium eutectique.

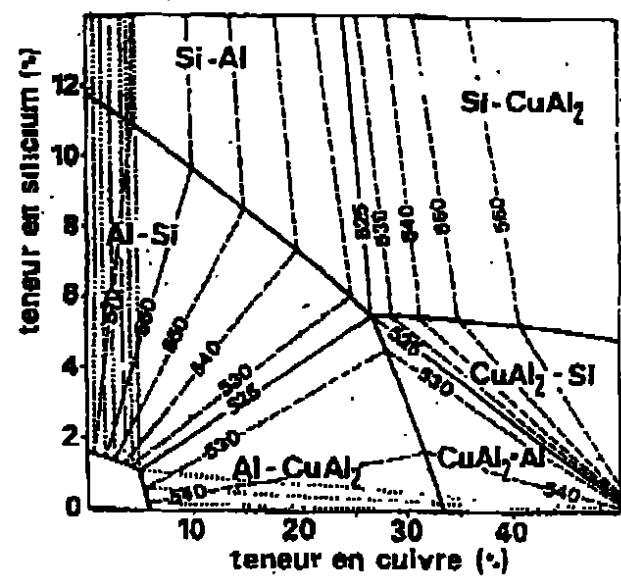
La vitesse de solidification joue également un rôle essentiel sur la structure du silicium eutectique. Une vitesse de solidification plus lente aura tendance à favoriser pour une même composition une structure plus grossière. Par contre, une solidification très rapide peut entraîner une structure modifiée même sans introduction de sodium ou de strontium.

EFFETS D'UNE ADDITION DE CUIVRE

En plus du silicium et du magnésium, une introduction de cuivre augmente encore la charge de rupture et la dureté après le traitement thermique de vieillissement. Toutefois,

l'amélioration de ces caractéristiques s'accompagne d'une diminution de la résistance à la corrosion.

L'interprétation du diagramme d'état du système ternaire «aluminium-silicium-cuivre» [4] montre (voir photo n° 1) qu'un alliage contenant 7 % de silicium et 4 % de cuivre est entièrement solidifié à 530°C et les conditions d'équilibre sont respectées, c'est-à-dire pour une vitesse de solidification et de refroidissement infiniment lentes.



1 - Représentation d'une partie du diagramme d'état du système ternaire aluminium-silicium-cuivre. D'après PHILIPPS [4].

En pratique les vitesses de solidification sont loin d'être négligeables. Si elles améliorent la répartition du silicium eutectique, elles provoquent également l'apparition d'un phénomène de ségrégation microscopique directe qui entraîne un enrichissement anormal en cuivre et en silicium du liquide.

(*) Communication présentée au 47^e Congrès National de Fonderie - Paris - Mai 1981.

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3 - Alliage à 7 % de silicium et 4 % de cuivre coulé en coquille froide - Remise en solution par un traitement de 8 heures à 540°C suivi d'une trempe à l'eau. Immersion de 2 minutes 30 dans le réactif d'attaque après polissage mécanique. Grains d'aluminium primaire représentés en A, plages d'eutectique ternaire en B et grains de silicium en C.

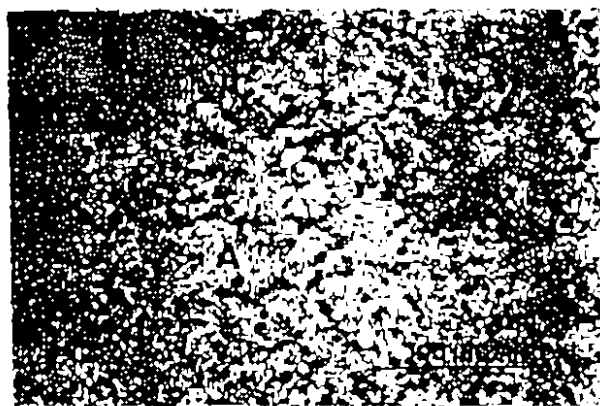
à l'eau. On y distingue les grains d'aluminium primaires, les grains de silicium et les plages d'eutectique ternaire colorées en jaune. Celles-ci, liquides à 540°C, sont solidifiées brutalement pendant la trempe.



4 - Alliage à 7 % de silicium et 2 % de cuivre coulé en coquille froide - Brut de coulée. Polissage mécanique suivi d'une immersion de 2 minutes 30 dans le réactif d'attaque. Les grains d'aluminium primaire sont représentés en A, les plages d'eutectique ternaire en B et l'eutectique binaire aluminium-silicium en C.

La photo n° 4 représente la microstructure d'un A-370 contenant 2 % de cuivre, brut de coulée en coquille froide. L'attaque met en évidence la présence de trois constituants : les grains d'aluminium primaires, l'eutectique binaire aluminium-silicium et quelques plages d'eutectique ternaire colorées en jaune-orangé, eutectique ternaire dont la présence s'explique par les phénomènes de ségrégation microscopique directe dont nous avons déjà parlé. La photo n° 5 représente la microstructure du même alliage à 2 % de cuivre après un traitement de remise en solution de huit heures à 540°C. Dans la matrice d'aluminium on constate la présence de grains arrondis de silicium tandis que les plages d'eutectique ternaire ont complètement disparu ce qui signifie que le cuivre est totalement remis en solution dans l'aluminium lors du traitement à haute température.

Afin de déterminer les meilleures conditions d'attaque et la composition optimale du réactif nous avons tenté d'expliquer le mécanisme de la coloration des phases. A cet effet un alliage à 6 % de silicium et à 10 % de cuivre a été élaboré. Pour une telle composition le diagramme ternaire «aluminium-silicium-cuivre» (voir photo n° 1) indique que la fin de solidification se situe nécessairement au point triple.



5 - Alliage à 7 % de silicium et 2 % de cuivre coulé en coquille froide - Remise en solution par un traitement de 8 heures à 540°C suivi d'une trempe à l'eau. Immersion de 2 minutes 30 dans le réactif d'attaque après le polissage mécanique. Matrice d'aluminium représentée en A et fine répartition de grains arrondis de silicium en C.

la composition chimique moyenne du dernier constituant métallographique qui apparaît est donnée par les coordonnées du point triple lui-même c'est-à-dire 88 % d'aluminium, 28,5 % de cuivre et 5,5 % de silicium.

INFLUENCE DE LA DURÉE DE L'ATTAQUE

L'observation microscopique de cet alliage plongé dans le réactif montre pour des temps d'attaque croissants une évolution nettement cyclique de la coloration des grains de silicium et des plages d'eutectique ternaire.

L'ensemble des micrographies (photos n° 6 à 14) illustre d'ailleurs très bien le phénomène. La première donne l'aspect de l'alliage après simple polissage mécanique. Les micrographies suivantes représentent la même plage pour des temps d'attaque de plus en plus longs, supérieure chaque fois de 30 secondes par rapport au précédent.

Les plages de silicium et de CuAl_2 identifiées initialement à la microsonde passent successivement par les teintes : bleu sombre, gris jaunâtre, bleu sombre, gris, violacé, gris verdâtre, gris verdâtre et gris pour le silicium et jaune pâle, violacé, jaune, rouge violacé, vert, brun, rouge violacé et gris pour le CuAl_2 . Pour un temps d'attaque supérieur à quatre minutes les deux phases ne peuvent plus être distinguées car elles apparaissent l'une et l'autre en gris.

Le caractère nettement cyclique que nous venons de mettre en évidence de la coloration rappelle étrangement les phénomènes d'interférence produits par une lame mince observée en lumière blanche polarisée dont on sait que la teinte varie avec son retard, lui-même fonction de son épaisseur [9], [10].

Ceci nous amène à formuler une première hypothèse pour expliquer l'apparition de plages colorées : au cours de l'immersion du métal dans le réactif il y aurait formation d'un dépôt transparent, dont l'épaisseur serait d'ailleurs fonction du temps d'attaque, sur le constituant le plus électropositif, dépôt qui provoque l'apparition de phénomènes d'interférence de la lumière blanche lors de l'observation au microscope.

COMPORTEMENT D'UNE STRUCTURE MONOPHASÉE

Pour vérifier cette hypothèse nous avons utilisé un dispositif expérimental qui, comme le montre le schéma de la photo n° 15, est une cellule d'électrolyse contenant le réactif d'attaque et dont l'originalité consiste à être composée d'une cathode sous forme d'une plaque circulaire parfaitement polie en acier inoxydable 18/8 de structure monophasée austénitique et d'une anode quasi ponctuelle constituée d'un fil de platine dont seule l'extrémité plonge dans la solution à l'aplomb du centre de la cathode.

Pour un temps d'électrolyse limité, la distance entre les

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de résiduel au détriment des grains d'aluminium primaires. En fin de solidification on obtient une phase interdendritique liquide à bas point de fusion dont la composition est donnée par les coordonnées du point triple. La présence d'autres éléments dans le métal, voir même d'impuretés, accentue encore le phénomène.

Ces alliages sont eux aussi susceptibles d'être traités thermiquement. La précipitation fine et homogène de composés intermétalliques dans la matrice, qui permet d'optimiser les caractéristiques mécaniques, a lieu pendant le traitement de revenu à basse température. La précipitation maximum impose un traitement préalable de remise en solution des éléments durcissants dans la matrice et ce à une température aussi élevée que possible, voisine en tout cas de la température de début de fusion de l'alliage.

Si les phénomènes de ségrégation microscopique directs ont été intenses lors de la solidification de la pièce, le risque de reliqufaction du constituant interdendritique riche en éléments d'addition est grand à la température de remise en solution, c'est une cause de brûlure.

Outre l'augmentation du risque d'apparition de « brûlures » pendant le traitement à haute température, la présence de ce constituant à bas point de fusion au sein du métal provoque une fragilisation importante de la pièce.

Pour mieux maîtriser les conditions d'apparition de ce constituant métallographique, son identification rapide et aisée parmi les autres phases s'avère indispensable.

EXAMEN STRUCTURAL - MISE AU POINT D'UN REACTIF SPECIFIQUE

L'examen métallographique d'alliages d'aluminium contenant 7 % de silicium se révèle délicat. En effet, la présence du silicium rend difficile, voire impossible, tout polissage électrolytique alors que le simple polissage mécanique montre une matrice d'aluminium ternaire et des grains de silicium grisâtres et sans relief.

TABEAU I

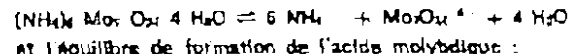
Composition de quelques réactifs révélant la structure des alliages aluminium-silicium

HF	0,5 cc
HCl	1,5 cc
HNO ₃	2,5 cc
H ₂ O	95,5 cc
(réactif de KELLER)	
HNO ₃	25,0 cc
H ₂ O	75,0 cc
NaF	0,5 gr
HNO ₃	1,0 cc
HCl	2,0 cc
H ₂ O	97,0 cc
CH ₃ COOH	30,0 cc
HNO ₃	70,0 cc
(NH ₄) ₂ Mo ₇ O ₂₄ + H ₂ O	2,5 gr
HNO ₃	10,0 cc
C ₂ H ₅ OH	190,0 cc

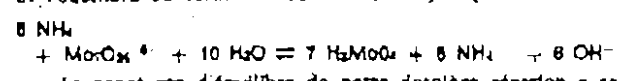
Faire un choix d'un réactif d'attaque est toujours une tâche délicate. On peut trouver dans la littérature la composition de nombreux réactifs qui révèlent plus ou moins bien la structure des alliages aluminium-silicium [5], [8]. Le tableau I en reprend quelques exemples.

On a même proposé un réactif à base de molybdate d'ammonium dissous dans un mélange alcool-acide nitrique qui colore le silicium de différentes manières selon les conditions d'attaque [7]. Cependant la préparation d'un tel réactif impose la dissolution du molybdate d'ammonium dans l'acide nitrique six fois normal, étape délicate si l'on veut éviter la précipitation d'acide molybdique.

En effet l'apparition d'acide molybdique est réglée à la fois par la réaction de dissociation du molybdate d'ammonium :



et l'équilibre de formation de l'acide molybdique :



La constante d'équilibre de cette dernière réaction a sa valeur fixée par la relation :

$$K_{eq} = \frac{[OH^-]^8 \cdot [H_2 MoO_4]^7}{[Mo_7 O_{21}^{4-}]}$$

On voit qu'une augmentation de la concentration en ions (OH⁻) dans le système déplace l'équilibre vers la gauche et limite la formation d'acide molybdique. Ceci prouve l'intérêt d'utiliser au départ une solution basique plutôt qu'acide pour faciliter la dissolution des cristaux de molybdate.

Ces considérations nous ont conduit à choisir un premier réactif contenant du molybdate d'ammonium et une quantité de soude telle que le p_H final est voisin de 8. Lorsque l'on souhaite utiliser cette solution pour révéler la structure des alliages aluminium-silicium contenant du cuivre, la température d'attaque doit être maintenue constamment à une valeur de 80°C durant l'immersion de l'échantillon. Cette condition est essentielle pour assurer une parfaite reproductibilité des teintures permettant l'identification aisée des différentes phases [8].

L'obligation de maintenir le réactif à cette température précise de 80°C et les difficultés que cela pose parfois au point de vue expérimental nous ont amené à revoir sa composition et à le modifier. En remplaçant le soude par du chlorure d'ammonium il s'avère que la mise en solution du molybdate est toujours aussi facile et que pour la composition suivante :

- 1 gr d'heptamolybdate d'ammonium
- 200 cc d'eau distillée
- 8 gr de chlorure d'ammonium

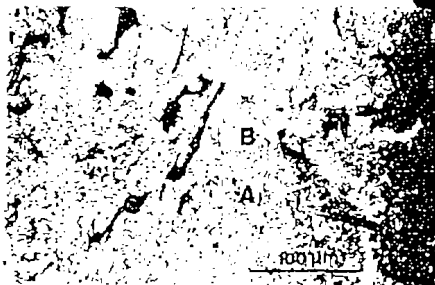
l'attaque peut s'effectuer simplement à la température ambiante. L'immersion de 2 minutes trente à 3 minutes dans cette nouvelle solution différencie parfaitement les grains de silicium et les plages d'eutectique ternaire qui apparaissent colorées respectivement en bleu sombre et en jaune.



2 - Alliage à 7 % de silicium et 4 % de cuivre coulé en coquille froide - Brut de coulée.

Polissage mécanique suivi d'une immersion de 2 minutes trente dans le réactif d'attaque. Grains d'aluminium primaire représentés en A et plages d'eutectique ternaire en B.

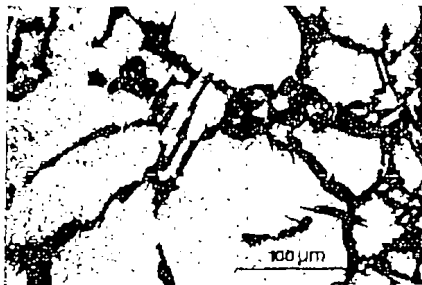
Voici d'ailleurs quelques exemples d'attaque obtenue sous ces conditions. On peut observer sur la photo n° 2 la microstructure d'un alliage contenant 4 % de cuivre et 7 % de silicium, brut de coulée en coquille froide. L'attaque révèle un constituant eutectique non résolu coloré en brun et les grains d'aluminium primaires. La photo n° 3 représente la microstructure du même alliage après un traitement de remise en solution de huit heures à 840°C suivi d'une trempe



6 - Alliage à 6 % de silicium et 10 % de cuivre - Solidification lente dans le creuset de fusion. Simple polissage mécanique sans attaque. On dénote déjà les grains d'aluminium en A, les plages de CuAl_2 en B et les grains de silicium en C.



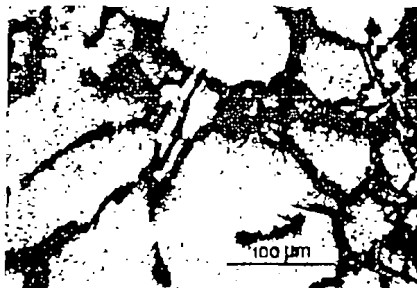
7 - Microstructure de la même plaque après 30 secondes d'attaque dans le réactif. On distingue les grains d'aluminium en A, les plages de CuAl_2 gris-jaunâtre en B et les grains de silicium bleu-noir en C.



8 - Microstructure de la même plaque après une minute d'attaque dans le réactif. Les grains de silicium sont devenus gris-brun, les plages de CuAl_2 violacées.



9 - Microstructure de la même plaque après 1 minute 30 d'attaque dans le réactif. Les grains de silicium sont devenus bleus, les plages de CuAl_2 jaunes.



10 - Microstructure de la même plaque après 2 minutes d'attaque dans le réactif. Les grains de silicium sont devenus gris et les plages de CuAl_2 rouge-violacé.



11 - Microstructure de la même plaque après 2 minutes 30 d'attaque dans le réactif. Les grains de silicium sont devenus violacés et les plages de CuAl_2 violetes.

160
-60

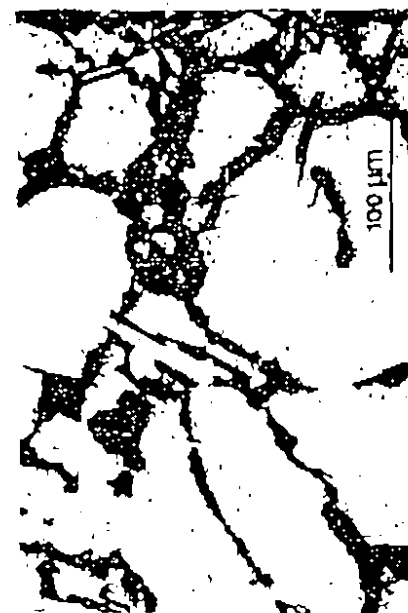
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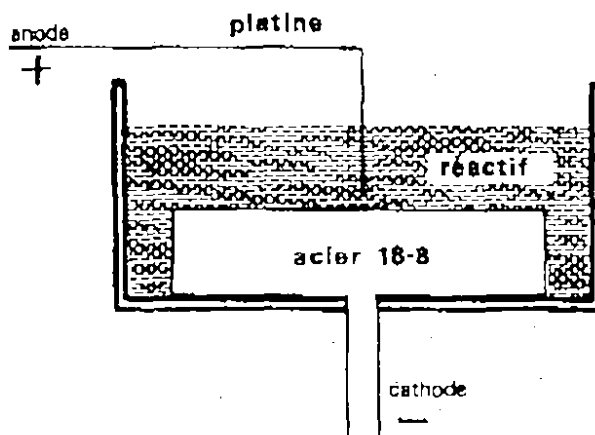
14 - Microstructure de la même place après 3 minutes d'attaque dans le réactif. Les grains de silicium et les plaques de CuAl_2 sont tous deux devenus gris et peuvent difficilement être distingués.



13 - Microstructure de la même place après 3 minutes d'attaque dans le réactif. Les grains de silicium sont devenus gris-vert et les plaques de CuAl_2 sont devenues grises.



12 - Microstructure de la même place après 3 minutes d'attaque dans le réactif. Les grains de silicium sont devenus gris et les plaques de CuAl_2 brunes.



15 - Dispositif expérimental d'électrolyse constitué d'une cellule contenant le réactif, d'une cathode polie en acier inoxydable 18/8 et d'une anode quasi ponctuelle.

électrodes croissantes du centre de la plaquette à sa périphérie provoque la formation d'un dépôt d'épaisseur variable diminuant progressivement du centre au bord de la cathode. Une telle surface observée en lumière blanche, à la lumière du jour par exemple, est recouverte d'anneaux concentriques colorés de périodicité manifeste (photo n° 16).



16 - Cathode en acier inoxydable recouverte du dépôt électrolytique (courant d'électrolyse 1 mA, durée de l'électrolyse 6 minutes) observée en lumière du jour. La réflexion sélective de la lumière blanche provoque l'apparition d'anneaux concentriques colorés.

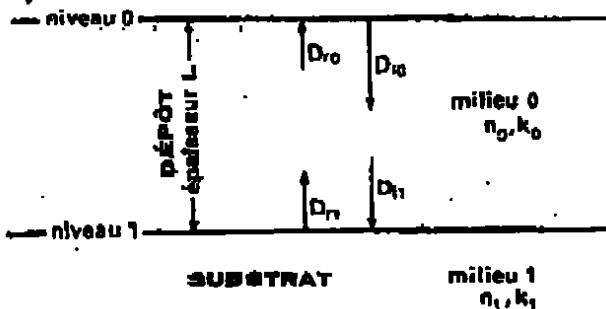
Par contre, pour de très longues durées d'électrolyse la cathode se recouvre d'un épais dépôt noirâtre qui s'écaille après séchage, s'enlève facilement et restitue la plaque d'acier inoxydable dans son état initial, parfaitement polie et non attaquée.

Ces essais confirment que l'utilisation du réactif provoque bien sur les zones cathodiques la formation d'un dépôt. Il reste à prouver qu'à une épaisseur donnée correspond une coloration précise.

La lumière blanche est composée d'ondes électromagnétiques planes et monochromatiques dont la longueur d'onde varie de 4.000 Å (dans le bleu) à 8.000 Å (dans le rouge).

La cathode recouverte du dépôt dont la représentation schématisée en un point donné figure à la photo n° 17 se comporte comme un système réfléchissant constitué par la superposition de deux milieux 0 et 1 la face inférieure de la lame ainsi formée est l'interface dépôt-substrat. Le dépôt électrolytique, milieu 0, est caractérisé par ses indices de réfraction n_0 et d'extinction k_0 , le substrat métallique l'est quant à lui par ses indices de réfraction n_1 et d'extinction k_1 .

161 161



17 - Modèle de système réfléchissant.
La face inférieure de la lame mince est l'interface
dépôt-substrat. $\vec{D}_0$ est le vecteur associé à l'onde
incidente au niveau 0, $\vec{D}_n$ est le vecteur associé
à l'onde réfléchie lorsqu'elle atteint le niveau 0.

Pour un tel modèle une onde incidente qui, au niveau 0,
peut se mettre sous forme :

$$\vec{D}_0 = a \cdot \vec{u}_0 \cdot \cos \omega t$$

Court dans le dépôt un chemin de longueur l correspon-
dant à son épaisseur.

Une onde électromagnétique qui se propage dans un
milieu isotrope absorbant a pour expression [9] :

$$\vec{D}_1 = a \cdot \vec{u} \cdot e^{-\frac{\omega k s}{c}} \cdot \cos \omega \left(t - \frac{s n}{c} \right)$$

relation dans laquelle

$\vec{D}_1$ est le vecteur associé à la propagation de l'onde

$a \cdot e^{-\frac{\omega k s}{c}}$ l'amplitude de l'onde après un parcours
 s dans le milieu d'indice d'extinction k

$$\omega = 2 \pi \cdot \nu = 2 \pi \frac{v}{\lambda} \quad \text{v valeur de la vitesse de la lumière dans le vide}$$

$\vec{u}_0$ vecteur unitaire

$a \cdot \cos \left(\omega \left(t - \frac{s n}{c} \right) \right)$ la phase de l'onde fonction du chemin
parcours s dans le milieu d'indice de
réfraction n

Au niveau 1 l'onde incidente après son parcours l dans le
milieu 0 aura pour expression :

$$\vec{D}_n = a \cdot \vec{u}_0 \cdot e^{-\frac{\omega k_0 l}{c}} \cdot \cos \omega \left(t - \frac{l n_0}{c} \right)$$

$$= a_1 \cdot \vec{u}_0 \cdot \cos \omega \left(t - \frac{l n_0}{c} \right)$$

en posant $a_1 = a \cdot e^{-\frac{\omega k_0 l}{c}}$

A l'interface dépôt-substrat métallique elle subit une
réflexion accompagnée d'un déphasage φ fonction des pro-
priétés optiques du dépôt et du substrat : elle est représen-
tée par

$$\vec{D}_n = \left[-a_1 \cdot \vec{u}_0 \cdot \cos \omega \left(t - \frac{l n_0}{c} \right) \right] \cdot \frac{n_1 - n_0}{n_1 + n_0}$$

Tous calculs faits (voir annexe) et compte tenu de ce
que dans la relation de MOYRE cos 0 représente la partie
réelle de ε cette valeur devient :

$$\vec{D}_n = \left[\text{partie réelle de } \left[-a_1 \cdot \frac{n_1 - n_0}{n_1 + n_0} \cdot e^{-\frac{\omega k_0 l}{c}} \right] \right] \cdot \vec{u}_0$$

ou encore

$$\vec{D}_n = -a_1 \cdot \sqrt{\varepsilon_1} \cdot \vec{u}_0 \cdot \cos \left[\omega \left(t - \frac{l n_0}{c} \right) - \varphi \right]$$

le pouvoir réflecteur r_1 à l'interface dépôt-substrat est don-
né par

$$r_1 = \frac{[(n_1^2 - n_0^2) + (k_1^2 - k_0^2)]^2 + 4(k_1 n_1 - k_0 n_2)^2}{(n_1 + n_0)^2 + (k_1 + k_0)^2}$$

et le déphasage à la réflexion φ défini par la relation :

$$\tan \varphi = \frac{2(k_1 n_0 - k_0 n_2)}{(n_1^2 - n_0^2) + (k_1^2 - k_0^2)}$$

L'onde réfléchie se propage à nouveau au travers du dé-
pôt où, au niveau 0, elle s'exprime par la relation :

$$\vec{D}_n = a_1 \cdot \sqrt{\varepsilon_1} \cdot \vec{u}_0 \cdot \cos \left[\omega \left(t - 2 \frac{l n_0}{c} \right) - \varphi \right]$$

$$= a \cdot \sqrt{\varepsilon_1} \cdot \vec{u}_0 \cdot \cos \left[\omega \left(t - 2 \frac{l n_0}{c} \right) - \varphi \right]$$

et vient interférer avec l'onde incidente au niveau 0 :

$$\vec{D}_0 = a \cdot \vec{u}_0 \cdot \cos \omega t$$

La résultante de ces deux ondes a une expression de la
forme :

$$\vec{D}_n = A \cos (\omega t + \phi) \cdot \vec{u}_0$$

Le flux lumineux associé à cette résultante est propor-
tionnel au carré de l'amplitude, c'est-à-dire :

$$I = \left[1 + r_1 \cdot e^{-\frac{4 \omega k_0 l}{c}} - 2 \cdot e^{-\frac{2 \omega k_0 l}{c}} \cdot \sqrt{\varepsilon_1} \cos \beta \right] (1)$$

avec $\beta = 2 \frac{\omega n_0 l}{c} + \varphi$

Lorsque, comme dans le cas qui nous concerne, le sub-
strat est de l'acier inoxydable, des simplifications impor-
tantes apparaissent dans l'expression du flux lumineux. En
effet il n'y a pas de déphasage à la réflexion et celle-ci est
totale à l'interface dépôt-substrat. Si de plus nous négli-
geons l'absorption dans le dépôt, ce qui est vrai pour les fai-
bles épaisseurs, la valeur du flux lumineux donnée par (1)
se réduit à

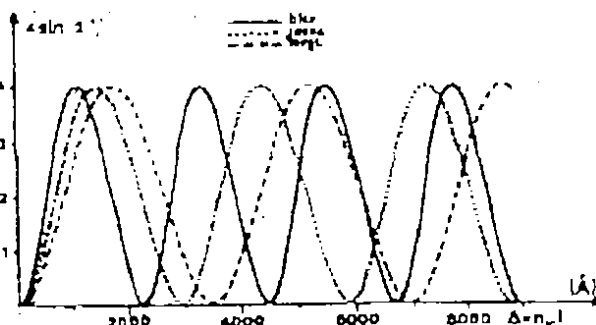
$$I = 4 \cdot \sin^2 2 \pi \frac{\Delta}{\lambda}$$

où λ est une longueur d'onde du spectre visible et Δ le re-
tard de la lame-dépôt.

Si nous portons en graphique (photo n° 16) ce facteur en
fonction du retard de la lame et donc en fonction de l'épais-
seur du dépôt, nous constatons la réflexion sélective des
composantes fondamentales de la lumière blanche : le bleu,
le jaune, le rouge dont les longueurs d'onde sont respective-
ment égales à 4500, 5800 et 7000 Å.

Variation du facteur $4 \sin^2 \frac{2\pi \Delta}{\lambda}$ en fonction de la longueur d'onde et du retard de la lame-dépôt

Δ (Å)	$\lambda_1 = 4.500 \text{ Å}$	$\lambda_2 = 5.890 \text{ Å}$	$\lambda_3 = 7.000 \text{ Å}$
0	0.000	0.000	0.000
400	1.123	0.883	0.484
800	3.231	2.271	1.732
1.200	3.956		3.102
1.600	2.484	3.928	3.928
2.000	0.488	2.882	3.802
2.400	0.172	1.208	2.788
2.800	1.930	0.086	1.382
3.200	3.766	0.289	0.283
3.600	3.818	1.855	0.832
4.000	1.653	3.258	0.763
4.400	0.377	3.999	2.090
4.800	0.882	3.370	3.382
5.200	2.749	1.803	3.892
5.600	3.883	0.371	3.518
6.000	3.000	0.088	2.445
6.400	0.882	1.078	1.052
6.800	0.019	2.725	0.128
7.200	1.382	3.881	0.128
7.600	3.439	3.748	1.052
8.000	3.878	2.418	2.445
8.400	2.209	0.801	3.818
8.800	0.304	0.008	3.992



18 - Représentation graphique du facteur $4 \sin^2 \frac{2\pi \Delta}{\lambda}$ en fonction du retard de la lame pour trois longueurs d'onde choisies dans le bleu (4.500 Å), le jaune (5.890 Å) et le rouge (7.000 Å). La résultante des réflexions sélectives justifie la formation des anneaux colorés sur la cathode en acier inoxydable.

On constate pour les très faibles épaisseurs une absorption de toutes les longueurs d'onde du spectre, la résultante sera donc un gris bluté puisque le bleu est toujours prédominant. Au fur et à mesure que l'épaisseur du dépôt augmente on peut prévoir par l'interprétation du graphique la succession des teintes suivantes : d'abord d'air par une possibilité de réflexion de toutes les composantes, puis jaune qui devient prédominant, violet résultant de la combinaison du rouge et du bleu, vert résultant du bleu et du jaune, jaune à nouveau dominant, violet combinaison du rouge et du bleu, et ainsi de suite... Pour des épaisseurs plus importantes les caractéristiques optiques du dépôt parviennent à masquer les phénomènes d'interférence.

Cette succession de teintes est bien celle que nous avons pu remarquer sur la cathode d'acier inoxydable après électrolyse (photo n° 17) et justifie ainsi notre explication du mécanisme de la coloration.

SYSTEME MULTIPHASE. - APPLICATION AUX A-57G

L'structure d'un échantillon d'A-57G contenant du cuivre, fraîchement poli et dégraissé, immergé de deux minutes trente à trois minutes dans la solution d'attaque à température ambiante est parfaitement révélée. Dans ces conditions un examen au microscope optique permet l'identification rapide des grains de silicium colorés en bleu et des plages d'austénite ternaire colorées en jaune.

Un tel alliage constitue un système multiphase formé d'une matrice d'aluminium accompagnée d'une ou plusieurs autres phases. Lorsqu'il est plongé dans la solution, un courant d'électrolyse interne compte-tenu des potentiels différents forme sur les phases plus électropositives que la matrice d'aluminium un dépôt adhérent qui, selon son épaisseur, provoque la réflexion sélective des composantes de la lumière blanche et donne des colorations différentes.

Pour les expliquer nous proposons le schéma réactif suivant sur la surface de l'échantillon immergé :

- 1) Lors de l'électrolyse interne un dépôt, vraisemblablement de sesquioxyde de molybdène hydraté, se forme à la surface de chacune des plages plus électropositives que la matrice d'aluminium, plus ou moins rapidement selon l'écart du potentiel qu'elle présente par rapport à cette phase.
- 2) Le dépôt initial isole le substrat de l'action du réactif mais il peut continuer à croître, son épaissement ultérieur est alors régi par la différence de potentiel qu'il présente lui-même par rapport à la matrice d'aluminium.
- 3) La couche déposée joue, lors de l'observation au microscope optique, le rôle d'une lame mince et provoque une réflexion sélective de la lumière blanche liée non seulement à l'épaisseur du dépôt mais aussi aux propriétés optiques du substrat. Les teintes observées, fonction de la durée de l'attaque, se justifient par l'épaisseur obtenue sous ces conditions et non par une coloration propre du dépôt.
- 4) Lorsque la différence de potentiel entre la matrice d'aluminium et une autre phase est insuffisante, la première étape du processus est difficile voire impossible à potentiel et la coloration de cette phase n'aura donc pas lieu.

CONCLUSIONS

L'application de la théorie des phénomènes d'interférence de la lumière blanche polarisée par une lame mince nous a permis d'avancer une explication de la coloration des phases silicium et CuAl_2 décelées lors de l'attaque métallographique par un réactif à base de molybdène d'ammonium dans les alliages hypoeutectiques «aluminium-silicium» contenant du cuivre.

L'utilisation d'un dispositif électrochimique original a révélé la formation sur le métal d'une pellicule dont l'épaisseur est directement fonction de la nature du substrat, de la durée de l'attaque et de la composition de l'électrolyte.

Une étude systématique de ces conditions nous amène à proposer la composition suivante pour la solution :

- 1 g d'heptamolybdate d'ammonium,
- 6 g de chlorure d'ammonium,
- 200 cc d'eau distillée

L'immersion des A-57G dans le réactif froid révèle sans ambiguïté les phases silicium et CuAl_2 par coloration sélective. Des précipités tels Al_3Ni , MgAl_2 , ... parfois présents dans d'autres alliages légers peuvent être identifiés par la même technique. Les observations ainsi faites ont chaque fois été confirmées par des examens complémentaires au microanalyseur afin de déterminer la corrélation : nature du précipité/coloration.

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ANNEXE

CALCUL DU FLUX LUMINEUX DANS UN SYSTEME LAME-SUBSTRAT

Une onde électromagnétique se propageant dans le vide peut se mettre sous la forme :

$$\vec{D} = a \cos \omega t \vec{u}_0 \text{ dans laquelle}$$

$\vec{D}$ est le vecteur associé à la propagation de l'onde,

a l'amplitude de l'onde

$\vec{u}_0$ un vecteur unitaire.

la pulsation $\omega = 2\pi \nu = \frac{2\pi c}{\lambda}$ (λ est la longueur d'onde, ν la fréquence).

t la phase de l'onde (où t représente le temps).

Le flux lumineux associé à cette onde est proportionnel à a^2 .

Un milieu absorbant isotrope est caractérisé par ses indices de réfraction n et d'extinction k ou par son indice complexe $m = n - jk$. L'expression de l'onde qui se propage dans un tel milieu aura cette fois la forme :

$$\vec{D} = a e^{-\frac{ka}{c}} \cos \omega \left(t - \frac{a}{c} \right) \vec{u}_0 \quad (1)$$

dans laquelle a est le chemin parcouru dans le milieu absorbant,

$a e^{-\frac{ka}{c}}$ est l'amplitude de l'onde (elle diminue quand a augmente).

$\omega \left(t - \frac{a}{c} \right)$ la phase de l'onde et c valeur de la vitesse de la lumière dans le vide.

Considérons le système réfléchissant représenté sur la figure n° 17. Il est constitué par la superposition de deux milieux 0 (épaisseur l) et 1 (substrat), caractérisés tous deux par leur indice complexe $m_0 = n_0 - jk_0$ et $m_1 = n_1 - jk_1$.

Soit une onde incidente traversant le milieu 0. Au niveau 0, elle peut se mettre sous la forme:

$$\vec{D}_i = a \cos \omega t \vec{u}_0 \quad (a \neq 0)$$

elle parcourt le milieu 0 (d'épaisseur l) et s'exprime au niveau 1 par une relation de la forme

$$\vec{D}_1 = a e^{-\frac{l}{c} k_0} \cos \omega \left(t - \frac{l}{c} \right) \vec{u}_0$$

$a = l$ dans la relation (1)

puisque $e^{j\alpha} = \cos \alpha + j \sin \alpha$ (relation de MOIVRE)

$\vec{D}_1$ = partie réelle de

$$[a e^{-\frac{l}{c} k_0} e^{j\omega \left(t - \frac{l}{c} \right)}] \vec{u}_0$$

Cette onde subit une réflexion à l'interface des milieux 0 et 1. Après réflexion elle peut s'exprimer [2] par une relation de la forme :

$$\vec{D}_r = - \frac{m_1 - m_0}{m_1 + m_0} \vec{D}_1 \quad (2)$$

ou encore :

$$\vec{D}_r = - a e^{-\frac{l}{c} k_0} \cos \omega \left(t - \frac{l}{c} \right) \vec{u}_0$$

$$\left(\text{partie réelle de } \frac{m_1 - m_0}{m_1 + m_0} e^{j\omega \left(t - \frac{l}{c} \right)} \right) \vec{u}_0 \quad (3)$$

or,

partie réelle de

$$\frac{m_1 - m_0}{m_1 + m_0} e^{j\omega \left(t - \frac{l}{c} \right)} = \text{partie réelle de} \frac{[(n_1^2 - n_0^2) + (k_1^2 - k_0^2) - 2j(k_1 n_0 - n_1 k_0)]}{(n_0 + n_1)^2 + (k_0 + k_1)^2} \cos \omega \left(t - \frac{l}{c} \right) + \frac{2(k_1 n_0 - n_1 k_0)}{(n_0 + n_1)^2 + (k_0 + k_1)^2} \sin \omega \left(t - \frac{l}{c} \right)$$

$$A \cos \omega \left(t - \frac{l}{c} \right) + B \sin \omega \left(t - \frac{l}{c} \right)$$

$$\text{en posant } A = \frac{(n_1^2 - n_0^2) + (k_1^2 - k_0^2)}{(n_0 + n_1)^2 + (k_0 + k_1)^2} \text{ et } B = \frac{2(k_1 n_0 - n_1 k_0)}{(n_0 + n_1)^2 + (k_0 + k_1)^2}$$

$$\text{et enfin est égal à : } r_1 \cos \left[\omega \left(t - \frac{l}{c} \right) - \varphi \right]$$

$$\text{si } r_1 \text{ est défini par la relation } r_1 = A^2 + B^2 \text{ et } \varphi \text{ par } \tan \varphi = \frac{B}{A}$$

En portant cette valeur dans la relation (3) l'expression de $\vec{D}_r$ devient :

$$\vec{D}_r = - a e^{-\frac{l}{c} k_0} r_1 \cos \left[\omega \left(t - \frac{l}{c} \right) - \varphi \right] \vec{u}_0 \quad (4)$$

Cette onde réfléchie, déphasée de φ par rapport à $\vec{D}_1$, retransverse le milieu 0 jusqu'au niveau 0. Son expression mathématique devient alors :

$$\vec{D}_r = - a e^{-\frac{l}{c} k_0} r_1 \cos \left[\omega \left(t - 2 \frac{l}{c} \right) - \varphi \right] \vec{u}_0 \quad (5)$$

Elle va interférer au niveau 0 avec l'onde incidente

$\vec{D}_i$. Le flux lumineux obtenu est proportionnel au carré de l'amplitude de la résultante de ces deux ondes

$$\vec{D}_{RU} = \vec{D}_i + \vec{D}_r$$

Sep. 1. 2004 11:25AM Fay Sharpe

Value de D_{no}

Comme $D_{in} = a \cos \alpha t \vec{u}_x$ et que la valeur de D_{no} est donnée par la relation (5), l'expression de $D_{no} = D_{in} + D_r$ devient :

$$D_{no} = a \left[\cos \alpha t - e^{-\alpha k_0 \frac{l}{c}} \cos \left[\alpha \left(t - 2 \frac{n_0}{c} \right) - \psi \right] \right] \vec{u}_x$$

$$= a [\cos \alpha t - e^{-\alpha k_0 \frac{l}{c}} \cos \alpha t \cos \beta - e^{-\alpha k_0 \frac{l}{c}} \sin \alpha t \sin \beta] \vec{u}_x$$

et on pose $\beta = 2 \pi \frac{n_0}{c} + \psi$

$$D_{no} = a [\cos \alpha t (1 - e^{-\alpha k_0 \frac{l}{c}} \cos \beta) - \sin \alpha t (e^{-\alpha k_0 \frac{l}{c}} \sin \beta)] \vec{u}_x$$

ou $D_{no} = a C \cos (\alpha t + \psi) \vec{u}_x$ (8)
expression dans laquelle ψ est défini par la relation :

$$\tan \psi = \frac{e^{-\alpha k_0 \frac{l}{c}} \sin \beta}{1 - e^{-\alpha k_0 \frac{l}{c}} \cos \beta}$$

et C par la relation :

$$C = \frac{1 - e^{-\alpha k_0 \frac{l}{c}} \cos \beta}{(1 - e^{-\alpha k_0 \frac{l}{c}} \cos \beta)^2 + (e^{-\alpha k_0 \frac{l}{c}} \sin \beta)^2}$$

Value du flux lumineux de la résultante D_{no}

L'amplitude de l'onde résultante est comme nous venons de le voir dans la relation (8) égale à $a \cdot C$. on peut donc en déduire que le flux lumineux est proportionnel au carré de cette valeur c'est-à-dire à $(a \cdot C)^2$ ou encore à :

$$a^2 \left[1 - 2 e^{-\alpha k_0 \frac{l}{c}} \cos \beta + e^{-2 \alpha k_0 \frac{l}{c}} \right] \quad (7)$$

Dans le cas favorable où l'absorption est faible c'est-à-dire où l'épaisseur l du dépôt est faible l'expression :

$$e^{-\alpha k_0 \frac{l}{c}}$$

devient négligeable. Si de plus la réflexion est

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totale à l'interface des milieux 0 et 1 $n_1 = 1$ et qu'il n'y a pas de déphasage à la réflexion $\psi = 0$, la valeur donnée par (7) est fortement simplifiée et devient :

$$a^2 \left(1 - 2 \cos 2\beta + \frac{n_0}{c} + 1 \right)$$

$$= a^2 \left[2 - 2 \cos^2 \alpha t - \frac{n_0}{c} \sin^2 \alpha t + \frac{n_0}{c} \right]$$

$$= 2 a^2 \left[\left(1 - \cos^2 \alpha t \right) \frac{n_0}{c} + \sin^2 \alpha t \frac{c}{n_0} \right]$$

$$= 4 a^2 \sin^2 \alpha t \frac{n_0}{c}$$

$$= 4 a^2 \sin^2 \frac{2\pi \Delta}{\lambda}$$

$$= 4 a^2 \sin^2 \frac{2\pi \Delta}{\lambda}$$

dans laquelle $\Delta = n_0 l$ est le retard de la lame.

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SOLUTION FOR CHEMICAL OXIDATION OF ALUMINUM AND ITS ALLOYS

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Committee of the Russian Federation
for Patents and Trademarks

DESCRIPTION OF INVENTION
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SOLUTION FOR CHEMICAL OXIDATION OF ALUMINUM AND ITS ALLOYS

[Rastvor dlya khimicheskogo oksidirovaniya aluminiya i ego splavov]

Inventors:	V. P. Bukreev et al.
Applicant:	Moscow Institute of Heat Engineering
References:	USSR Inventor's Certificate No. 455172, Cl. C 25 C 22/00, 1975 USSR Inventor's Certificate No. 539983, Cl. C 23 C 22/06, 1977

The invention relates to the chemical treatment of metals, specifically to chemical oxidation of items of aluminum and its alloys, and can be used in the production of radioelectronic equipment in the radioelectronic and other mechanical branches of industry.

The goal of the invention is a reduction of the electrical contact resistance of the coatings while simultaneously improving their protective properties.

The proposed solution contains, g/L:

Ammonium or alkaline metal phosphate	15-30
Ammonium or alkaline metal chloride	20-50

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Ammonium or alkaline metal citrate	10-25
Ammonium or alkaline metal molybdate	4-12
N,N'-Diphenylguanidine	0.2-0.6

The solution is prepared in the following way.

First the calculated quantities of all of the components are weighed out and dissolved (except for the molybdate) in warm (60-70°C) water in separate containers. N,N'-Diphenylguanidine is dissolved in slightly acidified water. Then the solutions of the phosphate, chloride and citrate are mixed together in succession. The mixture of solutions is mixed, acid is added (for example phosphoric or hydrochloric) to a pH of 1-3 and the molybdate salt is poured in. After the molybdate has dissolved the solution of N,N'-diphenylguanidine is added, the pH is corrected to 1-3, and the total volume of the solution is brought up to the required value with water.

The process of application of coatings includes the following stages.

First smooth plates measuring 50 x 20 x 2 mm of aluminum type AO and its alloys AMg-6 and D16 AT (surface roughness $R_a = 1.25 \mu\text{m}$) are degreased in the usual way in an organic solvent (for example gasoline) and in a solution containing disodium phosphate (10-15 g/L) and soda ash (5-7 g/L). Then the degreased plates are subjected to etching in a hydrochloric acid solution (100-120 g/L) at 50-60°C for 0.5-1.5 min and, after being washed in hot and cold water, are subjected to brightening at room temperature in a nitric acid solution (1:1) for 1-5 min. After a thorough washing, chemical oxidation of the samples is carried out. The oxidation time at room temperature is 20-60 min, depending on the composition of the solution, while at higher temperatures (for example, 80-90°C) it is 3-5 min. The oxidation process is stopped when the plates have reached a yellow or pale green color. The coated plates are washed in hot water and dried in a drying chamber.

The density of the single-use charge of solution is no more than $2.0 \text{ dm}^3/\text{L}$. In operation, the pH of the solution decreases, which leads to a significant slowing of the rate of the chemical oxidation process even before the solution is completely spent. In order to prevent a reduction of the rate of formation of the coatings, it is necessary to correct the pH periodically to the initial value.

The contact resistance of the oxide coatings is measured with an E6-18/1 milliohm meter by the four-wire scheme using current and voltage leads. For this purpose, two plates with the tested coating are put into a special holder of a dielectric material in which reliable contact between the plates with a strictly defined area (5 cm^2) is supported by a load of 100 g over the entire contacting surface. To connect the plates into the electrical circuit, knife electrodes, which are brought to the surface of the plates without contacting each other, are used.

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The protective properties of the coatings are determined by accelerated tests with the plates held in a 5% NaCl solution. Examination of the plates with a BMS-1 microscope (X4 magnification) is carried out once a day. If points of corrosion in the form of white bloom are found on the surface of the samples, the tests are stopped and the last 24 h are not counted in the test result.

The table gives the compositions of the tested solutions and the results of testing the oxide chemical coatings.

As the results show, the proposed solution supports the formation of coatings with low contact resistances (0.070-0.105 mOhm/cm²) compared with the known solution (0.310 mOhm/cm²), which improves their functional characteristics and makes it possible to use them in low-amperage cable connectors.

The better protective properties of the proposed coatings allow the coated articles to be used in a marine atmosphere that contains chlorides. An important advantage of the proposed solution is also the fact that it can work at room temperature, thereby simplifying the technological process.

The technical and economic advantages of the proposed solution are a reduction of the electrical contact resistance of the coatings while simultaneously improving their protective properties.

Claim

A solution for chemical oxidation of aluminum and its alloys, which contains an ammonium or an alkali metal phosphate and an ammonium or an alkali metal chloride, which is distinguished by the fact that, with the goal of reducing the electrical contact resistance of the coatings while simultaneously improving their protective properties, it additionally contains an ammonium or an alkali metal citrate, an ammonium or an alkali metal molybdate, and N,N'-diphenylguanidine in the following component ratios, g/L:

Ammonium or alkaline metal phosphate	15-30
Ammonium or alkaline metal chloride	20-50
Ammonium or alkaline metal citrate	10-25
Ammonium or alkaline metal molybdate	4-12
N,N'-Diphenylguanidine	0.2-0.6

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Химический состав и свойства растворов (1)	(2) Характеристики для состава														
	известно (3)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
(4) Составление растворов, г/л:															
Na ₂ CO ₃	3-5	20	15	-	20	-	20	-	25	-	30	30	15	20	20
K ₂ CO ₃	30-40	-	-	20	-	20	-	25	-	30	-	30	-	-	-
HCl	-	-	-	-	35	-	35	-	40	-	40	-	-	-	-
H ₂ SO ₄	-	40	30	30	-	35	-	40	-	-	50	-	30	40	40
Na ₂ SO ₄ · 10H ₂ O	-	5	10	-	15	-	20	-	20	-	20	25	25	30	30
(NH ₄) ₂ SO ₄	-	-	-	15	-	15	-	-	20	-	-	-	-	-	-
(NH ₄) ₂ CO ₃	-	5	4	-	4	-	8	-	-	10	12	12	12	10	-
K ₂ Cr ₂ O ₇	-	-	-	5	-	5	-	5	-	-	-	-	-	-	-
(C ₂ H ₅) ₂ SO ₄	-	0,1	0,2	0,3	0,3	0,4	0,3	0,5	0,4	0,6	0,6	0,6	0,7	-	0,5
Температура, °C	30	30	30	20	20	20	20	30	20	20	20	20	20	20	20
Время, мин	3	3	5	40	40	40	40	3	30	30	30	20	20	40	40
(5) Контактное сопротивление, мОм/см ²															
	0,110	0,260	0,105	0,305	0,096	0,075	0,070	0,070	0,070	0,045	0,090	0,090	0,245	0,130	0,170
(6) Защитные свойства, сут															
	2	3	6	7	7	8	9	9	9	8	8	6	6	5	3
(6) Образцы из алюминия марки АД, образцы из стали ИЛ6 АТ.															

(6) Образцы из алюминия марки А2.
Образцы из сплава Д16 АТ.

- Key: 1 Components of solution and properties of coatings
 2 Characteristics of composition
 3 Known
 4 Concentration of components, g/L:
 5 Temperature, °C
 Time, min
 Contact resistance, mOhm/cm²
 Protective properties, days
 6 Samples of aluminum type AO.
 Samples of alloy D16 AT.



СОЮЗ СОВЕТСКИХ
СОЦИАЛИСТИЧЕСКИХ
РЕСПУБЛИК

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ГОСУДАРСТВЕННЫЙ КОМИТЕТ
ПО ИЗОБРЕТЕНИЯМ И ОТКРЫТИЯМ
ПРИ ГКНТ СССР

ОПИСАНИЕ ИЗОБРЕТЕНИЯ

К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

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Авторское свидетельство СССР

№ 539983, кл. С 23 С 22/06, 1977.

(54) РАСТВОР ДЛЯ ХИМИЧЕСКОГО ОКСИДИРОВАНИЯ АЛЮМИНИЯ И ЕГО СПЛАВОВ

(57) Изобретение относится к химической обработке металлов, в частности к химическому оксидированию изделий из алюминия и его сплавов, и может быть использовано в

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производстве радиоэлектронной аппаратуры. Цель - снижение электрического переходного сопротивления покрытий при одновременном повышении их защитных свойств. Раствор содержит, г/л: фосфат аммония или щелочного металла 15 - 30, хлорид аммония или щелочного металла 20 - 50, цитрат аммония или щелочного металла 10 - 25, молибдат аммония или щелочного металла 4 - 12 и N, N'-дифенилгуанидин 0,2 - 0,6. Снижение электрического переходного сопротивления покрытий при одновременном повышении их защитных свойств достигается введением в состав раствора цитрата аммония или щелочного металла, молибдата аммония или щелочного металла и N, N'-дифенилгуанидина. 1 табл.

Изобретение относится к химической обработке металлов, в частности к химическому оксидированию изделий из алюминия и его сплавов, и может быть использовано в производстве радиоэлектронной аппаратуры в радиоэлектронной и других машиностроительных отраслях промышленности.

Цель изобретения - снижение электрического переходного сопротивления покрытий при одновременном повышении их защитных свойств.

Предлагаемый раствор содержит, г/л:

Фосфат аммония или щелочного металла 15 - 30

Хлорид аммония или щелочного металла 20 - 50

Цитрат аммония или щелочно-

го металла 10 - 25

Молибдат аммония или щелочного металла 4 - 12

N, N'-дифенилгуанидин 0,2 - 0,6

Приготовление раствора осуществляют следующим образом.

Сначала отвешивают расчетные количества всех компонентов и в отдельных емкостях растворяют их (кроме молибдата) в теплой (60 - 70°C) воде. N, N'-дифенилгуанидин растворяют в слегка подкисленной воде. Затем последовательно сливают вместе растворы фосфата, хлорида и цитрата. Смесь растворов перемешивают, доводят кислотой (например, фосфорной или соляной) до pH 1 - 3 и высыпают соль молибдата. После растворения молибдата вводят рас-

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твор N, N¹-дифенилгуанидина, корректируют до pH 1 – 3 и доводят водой общий объем раствора до необходимого значения.

Процесс нанесения покрытий включает в себя следующие стадии.

Сначала ровные пластины размером 50 x 20 x 2 мм из алюминия марки АО и его сплавов марки АМг-6 и Д16 АТ (шероховатость поверхности R_а = 1,25 мк) обезжиривают обычным способом в органическом растворителе (например, бензине) и в растворе, содержащем двухзамещенный фосфат натрия (10 – 15 г/л) и кальцинированную соду (5 – 7 г/л). Затем обезжиренные образцы подвергают травлению в растворе едкого натра (100 – 120 г/л) при 50 – 60°C в течение 0,5 – 1,5 мин и после промывки в горячей и холодной воде – осветлению при комнатной температуре в растворе азотной кислоты (1 : 1) в течение 1 – 5 мин. После тщательной промывки проводят химическое оксидирование образцов. Время оксидирования при комнатной температуре 20 – 60 мин в зависимости от состава раствора, а при более высоких температурах (например 80 – 90°C) – 3 – 5 мин. Процесс оксидирования прекращают при достижении желтого или светло-зеленого цвета образцов. Покрытые образцы промывают в горячей воде и сушат в сушильном шкафу.

Плотность одноразовой загрузки раствора составляет не более 2,0 дм²/л. В процессе работы значение pH раствора изменяется в сторону увеличения, что приводит к существенному замедлению скорости процесса химического оксидирования еще до выработки раствора. Для предотвращения снижения скорости образования покрытий необходимо периодически корректировать pH до исходного значения.

Переходное электрическое сопротивление оксидных покрытий измеряют с помощью миллиомметра Е6-18/1 по четырехпроводной схеме с использованием токовых и потенциальных проводников. С этой целью две пластины с исследуемым покрытием помещают в специальное приспособление из диэлектрического материала, в котором надежный контакт между пластинами со строго определенной площадью (5 см²) обеспечивается нагрузкой весом 100 г на всю контактирующую поверхность. Для включения пластин в электрическую схему используют ножевые электроды, которые подводят к поверхности пластин, не соприкасающихся между собой.

Защитные свойства покрытий определяют методом ускоренных испытаний с по-

мощью выдержки образцов в 5%-ном растворе NaCl. Осмотр образцов с помощью микроскопа БМС-1 (4-кратное увеличение) проводят один раз в сутки. В случае обнаружения на поверхности образцов точек коррозии в виде белого налета испытания прекращают и последние сутки в результате испытаний не засчитывают.

Составы опробованных растворов и результаты испытаний оксидных химических покрытий представлены в таблице.

Как показывают результаты опробования, предлагаемый раствор обеспечивает получение покрытий с более низким значением переходного сопротивления (0,070 – 0,105 мОм/см²) по сравнению с известным (0,310 мОм/см²), что улучшает их функциональные характеристики и позволяет использовать в слаботочных кабельных разъемах.

Более высокие защитные свойства предлагаемых покрытий допускают эксплуатацию покрываемых изделий в морской атмосфере, содержащей хлориды. Важным преимуществом предлагаемого раствора является и то, что он может работать при комнатной температуре, упрощая тем самым технологический процесс.

Технико-экономическим преимуществом предлагаемого раствора является снижение электрического переходного сопротивления покрытий при одновременном повышении их защитных свойств.

Формула изобретения

Раствор для химического оксидирования алюминия и его сплавов, содержащий фосфат аммония или щелочного металла и хлорид аммония или щелочного металла, отличающийся тем, что, с целью снижения электрического переходного сопротивления покрытий при одновременном повышении их защитных свойств, он дополнительно содержит цитрат аммония или щелочного металла, молибдат аммония или щелочного металла и N, N¹-дифенилгуанидин при следующем соотношении компонентов, г/л:

Фосфат аммония или щелочного металла	15 – 30
Хлорид аммония или щелочного металла	20 – 50
Цитрат аммония или щелочного металла	10 – 25
Молибдат аммония или щелочного металла	4 – 12
N, N ¹ -Дифенилгуанидин	0,2 – 0,6

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Компоненты раствора и свойства покрытий	Показатели для состава														
	известного		2	3	4 ^a	5	6	7 ^а	8	9	10	11	12	13	14
Содержание компонентов, г/л:															
Na ₂ PO ₄	3-5	20	15	-	20	-	20	-	25	-	30	30	25	20	20
K ₂ PO ₄	30-40	-	-	20	-	20	-	25	-	30	-	-	-	-	-
NaCl	-	-	-	-	35	-	35	-	40	40	-	50	-	-	-
NH ₄ Cl	-	40	30	30	-	35	-	40	-	-	50	-	50	40	40
Na ₂ S ₂ O ₅ · 5H ₂ O	-	8	10	-	15	-	20	20	-	20	25	25	30	20	20
(NH ₄) ₂ SO ₄ · H ₂ O	-	-	-	15	-	15	-	-	20	-	-	-	-	-	-
(NH ₄) ₂ SO ₄ · 0,4H ₂ O	-	3	4	-	6	-	8	-	-	10	12	12	13	10	-
K ₂ MoO ₄ · 10H ₂ O	-	-	-	6	-	6	-	8	8	-	-	-	-	-	-
(C ₂ H ₅ NH ₂) ₂ · C=NH	-	0,1	0,2	0,3	0,3	0,4	0,5	0,5	0,6	0,6	0,6	0,6	0,7	-	0,5
Температура, °С	90	90	80	20	20	20	20	90	20	20	20	20	20	20	20
Время, мин	3	3	5	60	60	60	40	3	30	30	20	20	20	40	40
Переходное сопротивление, мОм/см ²		0,310	0,260	0,105	0,095	0,090	0,075	0,070	0,070	0,085	0,090	0,090	0,245	0,330	0,290
Закрепитель свойства, сут	2	5	6	7	7	8	9	9	9	8	8	8	6	5	3

Образцы из алюминия марки А0.
Образцы из сплава Д16 АТ.

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173 173

1678900

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1

Изобретение относится к электролитическому нанесению покрытий, в частности к нанесению пассивных молибдатовых пленок на оцинкованную сталь.

Известен способ пассивирования цинковых покрытий путем химической обработки при $pH = 5,5 - 5,0$ и комнатной температуре в течение $0,5 - 1,5$ мин. в водном растворе, содержащем, г/л:

Молибдат аммония 5—8
Хлорид аммония 20—60 [1].

Недостатком данного способа является значительная продолжительность пассивирования.

Наиболее близким к изобретению является способ пассивирования цинковой поверхности, включающий обработку в водном растворе переменным током промышленной частоты при плотности тока

≥ 30 А/дм² ($30 - 80$ А/дм²)

и температуре раствора $35 - 60^\circ\text{C}$ [2].

Однако известный способ ведут в щелочном четырехкомпонентном растворе с использованием органических добавок, содержащем едкий натр, нитрат и нитрит натрия и алканолами. Пассивирование ведут в течение $7 - 90$ сек.

По известному способу на изделиях из чистого цинка получают пассивную пленку черного цвета толщиной $1,5 - 2$ мкм. Одна-

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ко ее коррозионная стойкость недостаточна.

Целью изобретения является повышение коррозионной стойкости.

Указанная цель достигается тем, что пассивирование ведут в водном растворе, содержащем, г/л:

Молибдат аммония 5—8
Хлорид аммония 20—60

10 Проволоку (или ленту) диаметром $0,5$ мм протягивают со скоростью $2 - 10$ м/мин через последовательно установленные ванны обезжиривания, травления, гальванического цинкования и пассивирования.

15 Пассивирование ведут при наложении переменного тока промышленной частоты плотностью $30 - 100$ А/дм² с бесконтактным подводом тока в растворе вышеуказанного состава при $pH = 5 - 5,5$ и температуре $35 - 60^\circ\text{C}$ в течение $3 - 20$ сек.

25 В результате такой обработки на поверхности оцинкованной проволоки формируется плотная пленка черного цвета, коррозионную стойкость которой оценивают как по времени появления очагов коррозии стальной основы, так и путем сравнения потенциалов с оксидной (известный спо-

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Таблица

Состав раствора, г/л режим и результаты обработки	Известный способ		Примеры		
	[1]	[2]	1	2	3
Молибдат аммония	5—8	щелочной раствор	5	8	8
Хлорид аммония	20—60		20	60	40
pH	5—5,5	11—12	5	5,5	5
Температура, °C	комнатная	30—60	35	60	50
Плотность тока, А/дм ²	—	30—80	30	100	50
Продолжительность, сек	60—90	7—90	5	7	20
Материал изделия	гальванически очищенный цинк	чистый цинк	гальванически оцинкованная сталь		
Количество цинка на изделии (г/дм ²) до пассивирования	210	210	210	210	210
После пассивирования	205	181—189	205,18	205,76	206,48
Толщина пассивной пленки, мкм	0,20	1,45—2,0	0,13	0,30	0,19
Коррозионная стойкость, (час) в 3%-ном растворе NaCl	4,1	2,05—2,8	6	6	6,5
В 5%-ном растворе CH ₃ COOH	1,3	0,130—0,165	7,7	8,0	7,9
Во влажной атмосфере при 40°C	240	144—172	265	282	300

соб) и молибдатной пленкой после обработки в 3%-ном растворе хлористого натрия (NaCl) (сразу после пассивирования и через 24 часа испытаний путем периодического погружения в 3%-ный раствор NaCl).

Испытания показывают, что электрохимическая активность цинкового покрытия после дополнительной обработки уменьшается в разной степени.

Потенциал цинкового покрытия, обработанного электрохимически в молибдатных растворах на 50—80 мВ положительнее потенциала непассивированного цинкового покрытия, а потенциал цинкового покрытия, обработанного в щелочном растворе, на 17÷25 мВ положительнее потенциала необработанного цинка, т. е. электрохимическая обработка в молибдатном растворе в большей степени снижает электрохимическую активность цинкового покрытия, через 24 часа испытаний разницы между потенциалами пассивированного и окисленного цинка составляет 33—55 мВ.

Изобретение может быть проиллюстрировано несколькими примерами, представленными в таблице.

Как видно из таблицы, изобретение позволяет значительно повысить коррози-

онную стойкость цинковой поверхности по сравнению с известными способами.

Кроме того, изобретение позволяет использовать операцию пассивирования в едином технологическом процессе нанесения цинкового покрытия.

Формула изобретения

Способ пассивирования цинковой поверхности, включающий обработку в водном растворе переменным током промышленной частоты при плотности тока ≥ 30 А/дм² и температуре 35—60°C, отличающийся тем, что, с целью повышения коррозионной стойкости, пассивирование ведут в водном растворе, содержащем:

Молибдат аммония	5—8
Хлорид аммония	20—60.

Источники информации.

принятые во внимание при экспертизе

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USSR Inventor's Certificate Patent No. 827613

METHOD OF PASSIVATING A ZINC SURFACE

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UNITED STATES PATENT AND TRADEMARK OFFICE
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METHOD OF PASSIVATING A ZINC SURFACE

[Sposob passivirovaniya tsinkovoi poverkhnosti]

Inventors:	N. A. Merekina and E. M. Romanova
Applicant:	All-Union Scientific Research Institute of the Hardware Industry

The invention relates to the electrolytic deposition of coatings, specifically to the deposition of passive molybdate films on zinc-plated steel.

There is a known method of passivating zinc coatings by chemical treatment at pH = 5.5-5.0 and room temperature over a period of 0.5-1.5 min in an aqueous solution containing, g/L:

Ammonium molybdate	5-8
Ammonium chloride	20-60 [1].

A shortcoming of this method is the significant length of the passivation process.

Closest to the invention is a method of passivating a zinc surface that includes treatment with industrial frequency AC current in an aqueous solution at a current density of $\geq 30 \text{ A/dm}^2$ ($30\text{-}80 \text{ A/dm}^2$) and a solution temperature of $35\text{-}60^\circ\text{C}$ [2].

However, the known method is carried out in an alkaline four-component solution using organic additives, which contains sodium hydroxide, sodium nitrate and nitrite and an alkanolamine. Passivation is carried out for 7-90 sec.

A passive black film $1.5\text{-}2 \text{ }\mu\text{m}$ thick is obtained on articles of pure zinc in the known method. However, the corrosion resistance of this film is insufficient.

The goal of the invention is an improvement of corrosion resistance.

This goal is achieved by the fact that passivation is carried out in an aqueous solution that contains, g/L:

Ammonium molybdate	5-8
Ammonium chloride	20-60.

A wire (or ribbon) 0.5 mm in diameter is drawn at a speed of 2-10 m/min through successive baths for degreasing, etching, electrolytic zinc plating, and passivation.

Passivation is carried out with the application of an industrial frequency AC current at a density of $30\text{-}100 \text{ A/dm}^2$ with noncontact feed of the current in a solution of the composition indicated above at $\text{pH} = 5\text{-}5.5$ and a temperature of $35\text{-}60^\circ\text{C}$ for 3-20 sec.

As a result of this treatment a dense black film forms on the surface of the zinc-plated wire; the corrosion resistance of the film is judged both from the time to appearance of foci of corrosion of the steel base and also by comparing the potentials with an oxide film (known method) and molybdate film after treatment in a 3% sodium chloride (NaCl) solution (immediately after passivation and after 24 h of testing by periodic immersion in a 3% NaCl solution).

Table

1	Состав раствора, г/л режим и результаты обработки	2 Известный способ		3 Примеры		
		11	12	1	2	3
4	Молибдат аммония	5-8	7	5	8	8
	Хлорид аммония	20-50	7	20	20	20
	pH	5-5,5	11-12	5	5,5	5
	Температура, °C	50-60	30-40	35	40	35
	Плотность тока, А/см²	—	20-30	30	100	30
	Продолжительность, сут	10-30	7-30	1	7	30
	Материал изделия	сталь	чистый металл	сталь		
	Количество цинка на изделие (г/м²) до пассивации	210	210	210	210	210
	Плотность пассивации	205	181-185	205,18	205,35	205,48
	Толщина пассивной пленки, мкм	0,20	1,48-2,0	0,13	0,30	0,19
	Коррозионная стойкость, (час) в 3%-ном растворе NaCl	4,1	2,05-3,5	6	6	4,5
	в 5%-ном растворе CH ₃ COOH	1,3	0,130-0,145	7,7	4,0	7,9
	во влажной атмосфере при 40°C	240	144-172	264	282	300

- Key:

1Composition of solution, g/L, conditions and treatment results
2Known method
3Examples
4Ammonium molybdate
Ammonium chloride
pH
Temperature, °C
Current density, A/cm²
Time, sec
Material of article
Amount of zinc on article (g/m²) before passivation
After passivation
Thickness of passive film, μm
Corrosion resistance (h) in 3% NaCl solution
In 5% CH₃COOH solution
In humid atmosphere at 40°C
5Room temperature
6Electrolytically zinc plated steel
7Alkaline solution
8Pure zinc

The tests show that the electrochemical activity of the zinc coating after the additional treatment decreases in differing degrees.

The potential of the zinc coating formed electrochemically in molybdate solutions is 50-80 mV more positive than the potential of the unpassivated zinc coating, while the potential of the zinc coating treated in the alkaline solution is 17-25 mV more positive than the potential

of the untreated zinc, i.e., electrochemical treatment in a molybdate solution lowers the electrochemical activity of the zinc coating to a greater degree; the difference between the potentials of the passivated and oxidized zinc after 24 h of testing is 33-55 mV.

The invention may be illustrated by means of several examples, which are presented in the table.

As can be seen from the table, the invention makes it possible to increase the corrosion resistance of the zinc surface substantially by comparison with the known methods.

In addition, the invention makes it possible to use the passivation operation in a unified technological process of application of the zinc coating.

Claim

A method of passivating a zinc surface, which includes treatment with AC voltage of industrial frequency in an aqueous solution at a current density $\geq 30 \text{ A/dm}^2$ and a temperature of 35-60°C, which is distinguished by the fact that, with the goal of improving the corrosion resistance, passivation is carried out in an aqueous solution that contains, g/L:

Ammonium molybdate	5-8
Ammonium chloride	20-60.

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Alloys³

Homes Et Fonderie, June-July, 1982, pp. 27-35
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ANALYSIS OF THE MECHANISM OF SELECTIVE COLORATION FACILITATING THE IDENTIFICATION OF VARIOUS PHASES IN ALUMINUM-SILICON-COPPER CASTING ALLOYS

Introduction

The use of silicon as an element added to aluminum to make molded parts has been known for a long time. Besides the range of ATS4G and ALS10G, foundry operators have had, for some ten years, a series of alloys containing 5-7% silicon which make it notably possible to obtain sealed parts without difficulty [1,2,3].

Besides this characteristic, AFS7s have good melting properties which can be explained by the shape of the "aluminum-silicon" equilibrium diagram, that is:

- small liquidus-solidus separation,
- high eutectic proportion, and
- low melting temperature.

The morphology of the solidification structure of the aluminum-silicon eutectic has a predominant influence on the mechanical properties of the alloys. The industrial hypoeutectic aluminum-silicon alloys essentially contain, in addition to the phosphorus impurity (from a few ppm to approximately 10 ppm), two elements: iron, an impurity originating from the electrolysis aluminum, and magnesium, the added element which is required for the obtention of good mechanical properties. Their structural effect during the solidification can be summarized as follows:

1) Addition of iron up to 1% has no detectable effect on the eutectic. It remains very finely lamellar.

2) Magnesium contents of approximately 0.3-0.6% which give it always an acicular form.

A modification treatment applied to the liquid metal by elements such as sodium, strontium or antimony is then necessary if one wishes to increase the mechanical characteristics of the alloy by a fine and dispersed distribution of the grains of eutectic silicon.

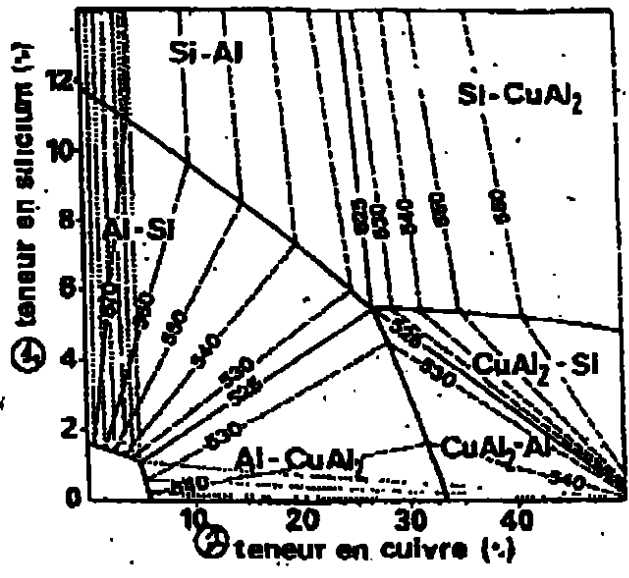
The rate of solidification plays also an essential role on the structure of the eutectic silicon. A slower solidification rate will tend to promote, for the same composition, a coarser structure. In contrast, very rapid solidification can result in a modified structure without the introduction of sodium or strontium.

Effect of the addition of copper

In addition to silicon and magnesium, an introduction of copper further increases the load upon rupture and the hardness after the thermal aging treatment. However, the improvement of these characteristics is accompanied by a decrease in the resistance to corrosion.

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The interpretation of this state diagram of the ternary system "aluminum-silicon-copper" [4] shows (see Photograph No. 1) that an alloy containing 7% silicon and 4% copper is entirely solidified at 530°C if the equilibrium conditions are respected, that is for infinitely slow rates of solidification and cooling.



1. Representation of a part of the state diagram of the ternary aluminum-silicon-copper system. According to Phillips [4].

- Key: 1 Silicon content (%)
- 2 Copper content (%)

In practice, the solidification rates are far from negligible. While they improve the distribution of the eutectic silicon, they also cause the appearance of a direct microscopic segregation effect which results in an abnormal enrichment in copper and silicon of the residual liquid to the detriment of the primary aluminum grains. At the end of the solidification, one obtains a liquid interdendritic phase with low melting point whose composition is given by the

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coordinates of the triple point. The presence of other elements in the metal, and even impurities, further accentuates this phenomenon.

These alloys are also capable of being thermally treated. The fine and homogeneous precipitation of intermetallic compounds in the matrix, which allows the optimization of the mechanical characteristics, takes place during the annealing treatment at low temperature. The maximum precipitation requires a prior treatment of re-dissolution of the hardening elements in the matrix, at the highest possible temperature, which, in any case, must be close to the temperature of the beginning of melting of the alloy.

While the direct microscopic segregation phenomena were intense during the solidification of the part, the risk of re-liquefaction of the interdendritic constituent which is rich in addition elements is high at the temperature of re-dissolution, and this causes burns.

Besides the increase of the risk of the appearance of "burns" during the treatment at high temperature, the presence of this constituent with low melting point inside the metal causes a considerable fragility of the part.

To better control the conditions of the appearance of this metallographic constituent, its rapid and easy identification among the other phases turns out to be indispensable.

Structural examination – development of a specific reactant

The metallographic examination of aluminum alloys containing 7% of silicon was shown to be tricky. Indeed, the presence of silicon makes any electrolytic polishing difficult, if not impossible, while simple mechanical polishing shows a matrix of lusterless aluminum and grayish silicon grains and without relief.

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Table I. Composition of several reactants revealing the structure of aluminum-silicon alloys

HF	0.5 cc
HCl	1.5 cc
HNO ₃	2.5 cc
H ₂ O	95.5 cc
(4) (réactif de KELLER)	
HNO ₃	25.0 cc
H ₂ O	75.0 cc
NaF	0.5 gr
HNO ₃	1.0 cc
HCl	2.0 cc
H ₂ O	97.0 cc
CH ₃ COOH	30.0 cc
HNO ₃	70.0 cc
(NH ₄) ₂ Mo ₇ O ₂₄ · 4 H ₂ O	2.5 gr
HNO ₃	10.0 cc
C ₂ H ₅ OH	190.0 cc

Key: 1 Keller reagent

It is always a delicate task to choose an etching reagent. In the literature, one can find the composition of numerous reactants which reveal the structure of aluminum-silicon alloys to varying degrees of satisfaction [5,6]. Table I shows some examples.

An ammonium molybdate based reagent has even been proposed, which is dissolved in a alcohol-nitric acid mixture which colors the silicon in different manners depending on the conditions of etching [7]. However, the preparation of such a reagent requires the dissolution of the ammonium molybdate in 6N nitric acid, which is a ticklish step if one wishes to prevent the precipitation of molybdic acid.

Indeed, the appearance of molybdic acid is governed both by the reaction of disassociation of ammonium molybdate:



and the equilibrium of formation of the molybdic acid:

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The equilibrium constant of the latter reaction has a value which is fixed by the relation:

$$K_{eq} = \frac{[\text{OH}^-]^6 \cdot [\text{H}_2\text{MoO}_4]^7}{[\text{Mo}_7\text{O}_{24}^{4-}]}$$

One can see that an increase in the concentration of (OH⁻) ions in the system displaces the equilibrium to the left and limits the formation of molybdic acid. This proves the advantage of using, at the beginning, a basic solution rather than an acidic solution to facilitate the dissolution of the molybdate crystals.

These considerations lead us to choose a first reagent containing ammonium molybdate and a quantity of sodium hydroxide such that the final pH is close to 6. If one wishes to use this solution to reveal the structure of copper containing aluminum-silicon alloys, the etching temperature must be constantly maintained at 80°C during the immersion of the sample. This condition is essential to assure perfect reproducibility of the hues which allow easy identification of the different phases [8].

The obligation of maintaining the reagent at this precise temperature of 80°C, and the difficulties which this raises sometimes from the experimental point of view, led us to review its composition and to modify it. By replacing the sodium hydroxide with ammonium chloride, it was shown that the dissolution of the molybdate is always easy and that for the following composition:

- 1 g ammonium heptamolybdate
- 200 cm³ distilled water
- 6 g ammonium chloride

the etching can be carried out simply at ambient temperature. Immersion for 2 min 30 s to 3 min in this new solution perfectly differentiates between silicon grains and ternary eutectic areas which appear colored in dark blue and yellow, respectively.

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2. Alloy of 7% silicon and 4% copper, cast in a cold mold – as cast.
Mechanical polishing followed by immersion for 2 min 30 s in the etching reagent. Primary aluminum grains represented at A and ternary eutectic areas at B.

Here are some examples of etching obtained under these conditions. One can observe, in Photograph No. 2, the microstructure of an alloy containing 4% copper and 7% silicon, as cast in a cold mold. The etching reveals an unresolved eutectic constituent colored in brown and the primary aluminum grains. Photograph No. 3 presents the microstructure of the same alloy after a treatment of re-dissolution for 8 h at 540°C followed by quenching in water. In the photograph, one can distinguish the primary aluminum grains, the silicon grains and the ternary eutectic areas colored in yellow. The latter, liquid at 540°C, are abruptly solidified during the quenching.

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3. Alloy with 7% silicon and 4% copper, cast in cold mold –
Re-dissolution by a treatment of 8 h at 540°C followed by quenching in water.
Immersion for 2 min 30 s in the etching reagent after mechanical polishing.
Primary aluminum grain represented at A, ternary eutectic areas at B and silicon grains at C.

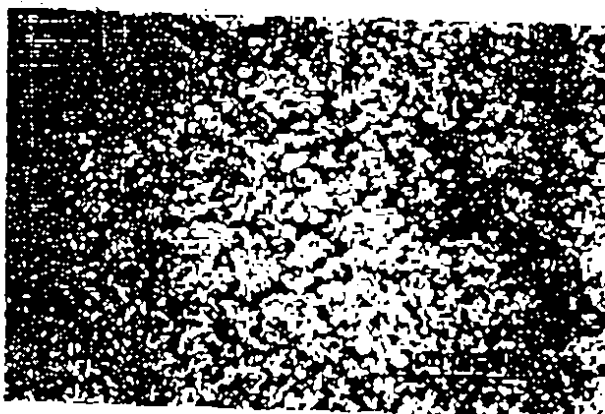


4. Alloy with 7% silicon and 2% copper, cast in cold mold – as cast.
Mechanical polishing followed by an immersion for 2 min 30 s in the etching reagent.
The primary aluminum grains are represented at A, the ternary eutectic areas at B, and the
aluminum-silicon binary eutectic at C.

Photograph No. 4 represents the microstructure of A-S7G containing 2% copper, as cast in a cold mold. The etching shows the presence of three constituents: primary aluminum grains, binary aluminum-silicon eutectic and a few areas of ternary eutectic of orange-yellow color,

where the presence of the ternary eutectic is explained by direct microscopic segregation events which we have already mentioned. Photograph No. 5 represents the microstructure of the same alloy at 2% copper after a treatment of re-dissolution for 8 h at 540°C. In the aluminum matrix, one notes the presence of rounded silicon grains, while the ternary eutectic areas have completely disappeared, which means that the copper is completely re-dissolved in the aluminum during the high-temperature treatment.

To determine the best conditions of etching and the optimum composition of the reagent, we attempted to make clear the mechanism of the coloration of phases. For this purpose, an alloy with 6% silicon and 10% copper was prepared. For such a composition, the ternary "aluminum-silicon-copper" diagram (see Photograph No. 1) indicated that the end of solidification is necessarily at the triple point; the average chemical composition of the later metallographic constituent which appears is given by the coordinates of the triple point itself, that is, 66% aluminum, 26.5% copper and 5.5% silicon.



5. Alloy with 7% silicon and 2% copper cast in cold mold – re-dissolution by a treatment of 8 h at 540°C followed by quenching in water.

Immersion for 2 min 30 s in the etching reagent after mechanical polishing.

Aluminum matrix is represented at A and a fine distribution of rounded silicon grains at C.

Influence of the duration of the etching

The microscopic observation of this alloy immersed in the reagent shows, for increasing etching times, a clearly cyclic variation of the coloration of the silicon grains and of the ternary eutectic areas.

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All the micrographs (Photographs No. 6-14) also illustrate this phenomenon very well. The first micrograph shows the appearance of the alloy after simple mechanical polishing, the following micrographs represent the same area for increasingly long etching times, each time longer by 30 s compared to the preceding one.

The areas of silicon and CuAl_2 which were initially identified with the microprobe successively go through the following hues: dark blue, yellow-gray, dark blue, gray, purplish, greenish-gray, greenish-gray [sic] and gray for silicon and straw yellow, purplish, yellow, purplish-red, green, brown, purplish-red and gray for CuAl_2 . For an etching time longer than 4 min, the two phases can no longer be distinguished because both have a gray appearance.

The clearly cyclic character which we have just shown for the coloration is strangely reminiscent of interference phenomenon produced by a thin blade which is observed under polarized white light and which is known to change its hue with the retardation which itself is a function of its thickness [9,10].

This leads us to formulate a first hypothesis to explain the appearance of colored areas: during the immersion of the metal in the reagent, it is thought that a transparent deposit forms, whose thickness would, moreover, be a function of the etching time, on the most electropositive constituent, which deposit causes the appearance of interference phenomena in white light during observation under the microscope.

Behavior of a monophase structure

To verify this hypothesis, we used an experimental setup which, as shown in the diagram of Photograph No. 15, is an electrolysis cell containing the etching reagent, whose originality consists in that it consists of a cathode in the form of a perfectly polished circular plate made of stainless steel 18/8 having an austenitic monophase structure and a nearly point-shaped anode consisting of a platinum wire whose one end is immersed in the solution straight above the center of the cathode.

For a limited electrolysis time, the distance between the electrodes, which increases from the center of the plate to its periphery, causes the formation of a deposit of varying thickness, with a progressive decrease of the thickness from the center to the edge of the cathode. Such a surface, observed in white light, for example in daylight, is covered with colored concentric rings of obvious periodicity (Photograph No. 16).



6. alloy with 6% silicon and 10% copper – slow solidification in the melting crucible.
Simple mechanical polishing without etching.
One can already see the aluminum grain at A, the CuAl_2 areas at B, and the silicon grains at C.



7. Microstructure of the same area after 30 s of etching in the reagent.
One distinguishes the aluminum grain at A, the gray-yellowish CuAl_2 areas at B, and the dark blue silicon grains at C.

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8. Microstructure of the same area after 1 min of etching in the reagent. The silicon grains have become gray-brown, and the CuAl_2 areas purplish.



9. Microstructure of the same area after 1 min 30 s of etching in the reagent. The silicon grains have turned blue, and the CuAl_2 areas yellow.

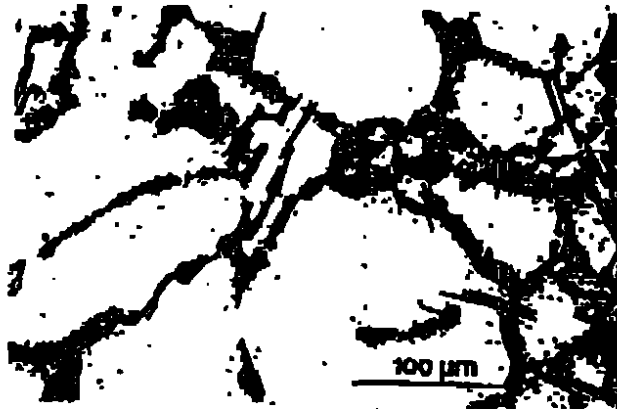


10. Microstructure of the same area after 2 min of etching in the reagent. The silicon grains have become gray and the CuAl_2 areas purplish-red.



11. Microstructure of the same area after 2 min 30 s of etching in the reagent. The silicon grains have become purplish and the CuAl_2 areas green.

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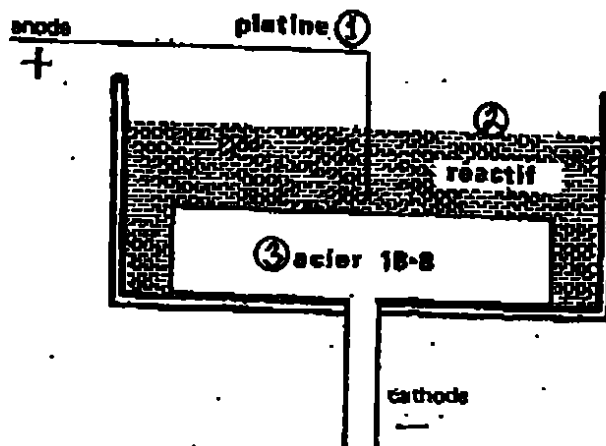
12. Microstructure of the same place [sic; area] after 3 min of etching in the reagent. The silicon grains have become gray and the CuAl_2 areas brown.



13. Microstructure of the same area after 3 min 30 s of etching in the reagent. The silicon grains have become greenish-gray and the CuAl_2 areas purplish red.



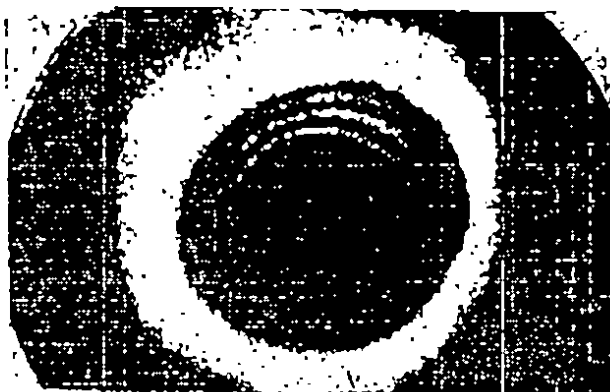
14. Microstructure of the same area after 4 min of etching in the reagent. The silicon grains and the CuAl_2 areas both have become gray and are difficult to distinguish.



15. Experimental electrolysis device consisting of a cell containing the reagent, a polished cathode made of stainless steel 18/8 and a nearly point-shaped anode.

Key: 1 Platinum
2 Reagent

3 Steel 18/8



16. Cathode made of stainless steel covered with the electrolytic deposit (electrolysis current 1 mA, duration of the electrolysis 6 min) observed in daylight. The selective reflection of the white light causes the appearance of colored concentric rings.

Moreover, for very long durations of electrolysis, the cathode is covered with a thick blackish deposit which flakes after drying, is easy to remove, and reconstitutes the plate of stainless steel in its initial, perfectly polished and unetched state.

These tests confirm that the use of the reagent indeed causes the formation of deposits on the cathodic zones. It remains to be proved that a given thickness corresponds to a precise coloration.

The white light consists of planar and monochromatic electromagnetic waves whose wavelength varies from $4000 \text{ \AA}$ (in the blue range) to $8000 \text{ \AA}$ (in the red range).

The cathode, which is covered with the deposit, of which a schematic representation at a given point is given in Photograph No. 17, behaves like a reflecting system consisting of the superposition of two media, 0 and 1, the lower face of the plate so formed is the deposit-substrate interface. The electrolytic deposit, medium 0, is characterized by its indexes of reflection n_0 and of extinction k_0 , while the metallic substrate is characterized by its indexes of refraction n_1 and of extinction k_1 .

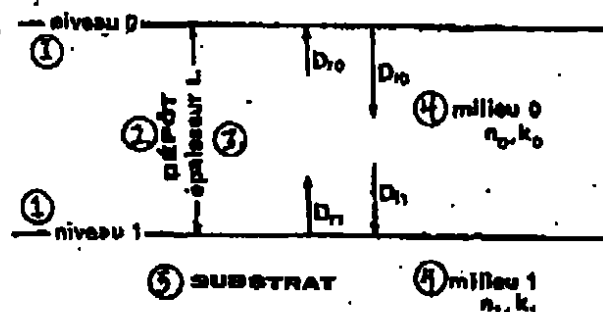


Figure 17. Model of reflecting system.

The lower face of the thin blade is the deposit-substrate interface. $\vec{D}_0$ is the vector associated with the wave which is incident at level 0, $\vec{D}_1$ is the vector associated with the reflected wave when it reaches the level 0.

- Key: 1 Level __
2 Deposit
3 Thickness L
4 Medium __
5 Substrate

For such a model, an incident wave which, at level 0, can be in the form:

$$\vec{D}_0 = a \cdot \vec{u}_0 \cdot \cos \omega t$$

travels in the deposit along a path of length l corresponding to its thickness.

An electromagnetic wave which propagates in an absorbing isotropic medium has the expression [9]:

$$\vec{D}_1 = a \cdot \vec{u}_1 \cdot \frac{\omega k l}{c} \cdot \cos \omega \left(t - \frac{s n}{c} \right)$$

in which relation $\vec{D}_1$ is the vector associated with the propagation of the wave

$$\frac{\omega k s}{c}$$

$a \cdot e$ the amplitude of the wave after traveling a path s in the medium with extinction index k

$$\omega = 2\pi \cdot \nu = 2\pi \frac{c}{\lambda}$$

c is the value of the speed of light in vacuum

$\vec{u}$, unit vector

$$\cos \omega \left(t - \frac{s n}{c} \right)$$

the phase of the wave, which is a function of the path traveled s in the medium of index of refraction n .

At level 1 the incident wave, after having traveled along path l in the medium 0, will have the following expression:

$$\begin{aligned} \vec{D}_1 &= a \cdot e^{-\frac{\omega k l}{c}} \cdot \vec{u}_0 \cdot \cos \omega \left(t - \frac{l n_0}{c} \right) \\ &= a_1 \cdot \vec{u}_0 \cdot \cos \omega \left(t - \frac{l n_0}{c} \right) \end{aligned}$$

$$\text{let } a_1 = a \cdot e^{-\frac{\omega k l}{c}}$$

At the deposit-metallic substrate interface, it undergoes a reflection accompanied by a phase shift ϕ which is a function of the optical properties of the deposit and of the substrate: it is represented by

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$$\vec{D}_1 = \left[-a_1 - \frac{m_1 - m_0}{m_1 + m_0} \right] \cdot \vec{u}_0 \cdot \cos \omega \left(t - \frac{l}{c} \right)$$

After all the calculations have been made (see appendix), and taking into account the fact that in the MOIVRE relation $\cos 0$ represents the real part of $e^{i \cdot 0}$, this value becomes:

$$\vec{D}_1 =$$

the real part of

$$\left[-a_1 - \frac{m_1 - m_0}{m_1 + m_0} \right] \cdot \vec{u}_0 \cdot \cos \omega \left(t - \frac{l}{c} \right)$$

or

$$\vec{D}_1 = -a_1 - \frac{m_1 - m_0}{m_1 + m_0} \cdot \vec{u}_0 \cdot \cos \left[\omega \left(t - \frac{l}{c} \right) - \varphi \right]$$

the reflecting capacity r_1 at the deposit-substrate interface is given by

$$r_1 = \frac{[(m_1^2 - n_0^2) + (k_1^2 - k_0^2)]^2 + 4(k_1 n_0 - k_0 m_1)^2}{[(m_1 + n_0)^2 + (k_1 + k_0)^2]^2}$$

and the phase shift at reflection, φ , is defined by the relation:

$$\textcircled{A} \quad \tan \varphi = \frac{2(k_1 n_0 - k_0 m_1)}{(m_1^2 - n_0^2) + (k_1^2 - k_0^2)}$$

Key: A tan

The reflected wave again is propagated through the deposit where, at level 0, it is expressed by the relation:

$$\begin{aligned}\vec{D}_m &= -a_1 \cdot \vec{r}_m \cdot e^{-i\left(\omega t - 2\frac{\omega k_0 l}{c} - \varphi\right)} \\ &= -a_1 \cdot \vec{r}_m \cdot e^{-i\left(\omega t - 2\frac{\omega k_0 l}{c} - \varphi\right)}\end{aligned}$$

and it interferes with the incident wave at level 0:

$$\vec{D}_0 = a \cdot \vec{u}_0 \cdot \cos \omega t$$

The resultant of these two waves has an expression of the form:

$$\vec{D}_R = A \cos (\omega t + \phi) \cdot \vec{u}_0$$

The light flux associated with this result is proportional to the square of the amplitude, that is:

$$a^2 \left[1 + r^2 - 2r \cos \beta \right]$$

with $\beta = 2 \frac{\omega k_0 l}{c} + \varphi$

When, as in the case which concerns us, the substrate is stainless steel, important simplifications can be made in the expression for the light flux. Indeed, there is no phase shift at reflection, and the reflection is total at the deposit-substrate interface. If, in addition, we neglect the absorption in the deposit, which is valid for the low thicknesses, the value of the luminous flux given by (1) is reduced to

$$4 \cdot \pi^2 \cdot \sin^2 2 \approx \frac{\Delta}{\lambda}$$

where λ is a wavelength of the visible spectrum and Δ the retardation of the blade-deposit.

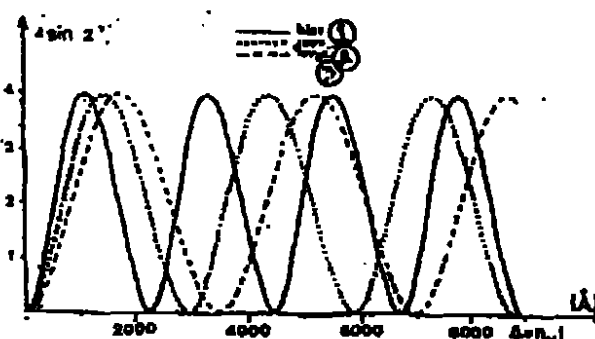
If we graph (Photograph No. 18) this factor as a function of the retardation of the blade and thus as a function of the thickness of the deposit, we observe the selective reflection of the fundamental components of the white light: the blue, the yellow, the red whose respective wavelengths are equal to 4500, 5890 and 7000 Å.

Table II

Variation of the factor $4 \sin^2 \frac{2\pi\Delta}{\lambda}$ as a function of the wavelength and the retardation of the blade-deposit

Δ (Å)	$\lambda_1 = 4.500 \text{ Å}$	$\lambda_2 = 5.890 \text{ Å}$	$\lambda_3 = 7.000 \text{ Å}$
0	0.000	0.000	0.000
400	1.123	0.883	0.484
800	3.231	2.271	1.732
1,200	3.856		3.102
1,600	2.484	3.828	3.828
2,000	0.468	2.882	3.802
2,400	0.173	1.306	2.788
2,800	1.830	0.081	1.382
3,200	3.788	0.288	0.283
3,600	3.818	1.553	0.082
4,000	1.683	3.234	0.783
4,400	0.077	3.888	2.060
4,800	0.882	3.370	3.383
5,200	2.749	1.803	3.862
5,600	3.896	0.371	3.818
6,000	3.000	0.083	2.446
6,400	0.882	1.872	1.032
6,800	0.019	2.725	0.128
7,200	1.382	3.881	0.128
7,600	3.438	3.748	1.052
8,000	3.879	2.418	2.446
8,400	2.208	0.801	3.818
8,800	0.304	0.008	3.882

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18. Graphic representation of the factor $4 \sin^2 \frac{2\pi\Delta}{\lambda}$ as a function of the retardation of the blade for three chosen wavelengths of blue (4500 Å), yellow (5890 Å) and red (7000 Å). The resultant of the selective reflection explains the formation of the colored rings on the cathode made of stainless steel.

Key: 1 Blue
Yellow
Red

One notes for very small thicknesses absorption of all the wavelengths of the spectrum, the resultant will thus be a bluish-gray, since blue always predominates. As the thickness of the deposit increases, one can predict by interpreting the graph the succession of the following tints: first clear, due to the possibility of reflection of all of the components, then yellow, which become predominant, purple, resulting from the combination of red and blue, green, resulting from the combination of blue and yellow, again yellow dominant, purple, combination of red and blue, and so on . . . For large thicknesses, the optical characteristics of the deposit succeed in masking the interference phenomena.

This succession of tints is indeed the one which we observed on the cathode made of stainless steel after electrolysis (Photograph No. 17) and it thus justifies our explanation of the mechanism of coloration.

Multiphase system – application to A-S7G

The structure of a sample of AS7G containing copper, which has been freshly polished and degreased, and has been immersed for 2 min 30 s to 3 min in the etching solution at ambient temperature, is perfectly revealed. Under these conditions, an examination under an optical microscope allows the rapid identification of the silicon grains colored in blue and the ternary eutectic areas colored in yellow.

Such an alloy constitutes a multiphase system formed from an aluminum matrix accompanied by one or more other phases. When it is immersed in the solution, an internal electrolysis current, taking into account the different potentials, forms on the phases which are more electropositive than the aluminum matrix, an adhering deposit which, depending on its thickness, causes the selective reflection of the components of white light and produces the different colorations.

To explain them, we propose the following reactive scheme on the surface of the immersed sample:

1) During the internal electrolysis, a deposit, probably a hydrated molybdenum sesquioxide, forms on the surface of every area which is more electropositive than the aluminum matrix, at varying speeds, depending on the difference in potential which it presents compared to this phase.

2) The initial deposit isolates the substrate from the action of the reagent, but it can then continue to increase, its subsequent thickness is then governed by the difference in potential which it presents compared to the aluminum matrix.

3) The deposited layer plays, during the observation under the optical microscope, the role of a thin blade, and it causes a selective reflection of the white light which is not only connected with the thickness of the deposit, but also with the optical properties of the substrate. The hues observed, which are a function of the duration of the etching, are explained by the thickness obtained under these conditions and not by an intrinsic coloration of the deposit.

4) When the difference in potential between the aluminum matrix and another phase is insufficient, the first step of the process is difficult, if not impossible, to obtain and the coloration of this phase will thus not take place.

Conclusions

The application of the theory of interference phenomena of polarized white light caused by a thin layer allowed us to propose an explanation for the coloration of silicon and CuAl_2 phases detected during metallographic etching by a reagent based on ammonium molybdate in hypoeutectic "aluminum-silicon" alloys containing copper.

The use of an original electrochemical device revealed the formation on the metal of a film whose thickness is a direct function of the nature of the substrate, the duration of the etching and the composition of the electrolyte.

A systematic study of these conditions leads us to propose the following composition for the solution:

1 g ammonium heptamolybdate,
6 g ammonium chloride,
200 cm³ distilled water.

The immersion of A-S7G in cold reagent reveals, without ambiguity, the silicon and CuAl₂ phases by selective coloration. Precipitates such as Al₃Ni, MgAl₂, . . . which are sometimes present in other light alloys can be identified by the same technique. The observations which have thus been made were each time confirmed by additional examinations with a microanalyzer to determine the correlation: nature of the precipitate/coloration.

* * *

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

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MARK E. BANDY
FAY, SHARPE, FAGAN, MINNICH & MCKEE, LLP
1100 SUPERIOR AVENUE, SUITE 700
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WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

Date of mailing
(day/month/year) **13 OCT 2004**

Applicant's or agent's file reference

FOR FURTHER ACTION

See paragraph 2 below

MCII20002PCT

International application No.

International filing date (day/month/year)

Priority date (day/month/year)

PCT/US04/17786

04 June 2004 (04.06.2004)

05 June 2003 (05.06.2003)

International Patent Classification (IPC) or both national classification and IPC

IPC(7): B32B 15/04; C23C 22/40, 68, 82; C23F 11/00; C09K 13/04 and US Cl.: See Electronic data bases.

Applicant

PEARCE ET AL.

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

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

2. FURTHER ACTION

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

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

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

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

Name and mailing address of the ISA/ US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Matthew A. Thexton

Telephone No. 571-272-1125

Form PCT/ISA/237 (cover sheet) (January 2004)

"DOCKETED"

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

207
International application No.

PCT/US04/17786

Box No. I Basis of this opinion

1. With regard to the language, this opinion has been established on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This opinion has been established on the basis of a translation from the original language into the following language _____, which is the language of a translation furnished for the purposes of international search (under Rules 12.3 and 23.1(b)).

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

a. type of material

☐ a sequence listing

☐ table(s) related to the sequence listing

b. format of material

☐ in written format

☐ in computer readable form

c. time of filing/furnishing

☐ contained in international application as filed.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority for the purposes of search.

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

4. Additional comments:

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US04/17786

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees the applicant has:
- ☒ paid additional fees
 - ☐ paid additional fees under protest
 - ☐ not paid additional fees
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is
- ☐ complied with
 - ☒ not complied with for the following reasons:
See the lack of unity section of the International Search Report (Form PCT/ISA/210)

4. Consequently, this opinion has been established in respect of the following parts of the international application:

- ☒ all parts.
- ☐ the parts relating to claims Nos. _____

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US04/17786

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

1. Statement

Novelty (N)	Claims <u>8-15,17,25</u>	YES
	Claims <u>1-7,16,18-24</u>	NO
Inventive step (IS)	Claims <u>17</u>	YES
	Claims <u>8-15,25</u>	NO
Industrial applicability (IA)	Claims <u>1-25</u>	YES
	Claims <u>NONE</u>	NO

2. Citations and explanations:
Please See Continuation Sheet

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US04/17786

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the questions whether the claims are fully supported by the description, are made:

Claims 1-25 are objected to as lacking clarity under PCT Rule 66.2(a)(v) because of the claims being not fully supported by the description. The description does not disclose the claimed invention in a manner sufficiently clear and complete for the claimed invention to be carried out by a person skilled in the art because: The formulations are not described as to the basis upon which they are to be created; i.e., weight percent, volume percent, mol percent, or otherwise.

Claims 1-25 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because claims 1-25 are indefinite for the following reason(s): The claimed formulations are not specified as to the basis upon which they are to be created; i.e., weight percent, volume percent, mol percent, or otherwise.

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

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International application No.
PCT/US04/17786

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

V. 2. Citations and Explanations:

Claims 1-7 lack novelty under PCT Article 33(2) as being anticipated by Shipley, Jr., et al. (US 3650957). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate (column 4, line 74 to column 5, line 65; examples 12, 13, and 19). Concentrations are "about" 1:1 (claims 8-10) and 2.5 percent, as required by the claims.

Claims 1-7, 16, 18-24 lack novelty under PCT Article 33(2) as being anticipated by Mitchell et al. (US 3314811). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate at "about" 1:1 by weight (column 3, lines 8-18), concentration determined at "about 1 ounce to about 3 pounds" per gallon of water (there are 8.34 pounds per gallon of water) (see claim 1) is "about" 2.5 percent, as required by claims 1-7. Such are for blackening aluminum substrates. Coated substrates with corrosion resistance are disclosed, as required by claims 16 and 18-24.

Claims 1-7, 16, 18-24 lack novelty under PCT Article 33(2) as being anticipated by Lewis et al. (US 2554256). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate at "about" 1:1 by weight and concentration of "about" 2.5 percent (column 4, lines 15-18), as required by the claims. Such are for coloring aluminum substrates. Coated aluminum substrates with corrosion resistance are disclosed (column 3, lines 52-55), as required by claims 16 and 18-24.

Claims 1-7, 16, and 18-24 lack novelty under PCT Article 33(2) as being anticipated by Belkin et al. (SU 1678900 A1, as evidenced by USPTO obtained translation). The reference discloses aqueous formulations of ammonium chloride and ammonium molybdate at "about" 1:1 and "about" 2.5 percent, as required by claims 1-7. Aluminum substrates are coated to provide corrosion protection, as required by claims 16 and 18-24.

Claims 1-7, 16, and 18-24 lack novelty under PCT Article 33(2) as being anticipated by Merekina et al. (SU 827613 B, as evidenced by USPTO obtained translation). The reference discloses aqueous formulations of ammonium chloride and ammonium molybdate at "about" 1:1 and "about" 2.5 percent, as required by claims 1-7. Zinc substrates are coated to provide corrosion protection, as required by claims 16 and 18-24.

Claims 8-15 lack an inventive step under PCT Article 33(3) as being obvious over Shipley, Jr., et al. (US 3650957). The reference discloses that the source of the complexing molybdenum compound is not critical (column 5, lines 15-18). Thus, it would have been obvious to the ordinary artisan to employ any commercially available molybdate, such as heptamolybdate.

Claims 8-15 and 25 lack an inventive step under PCT Article 33(3) as being obvious over Mitchell et al. (US 3314811) in view of Paulet (US 4018628). The Paulet reference is directed to formulations for blackening aluminum, as is the Mitchell reference. The Paulet reference discloses ammonium molybdate or heptamolybdate (column 2, lines 4-7). It would have been obvious to the ordinary artisan to modify the formulations of the Mitchell reference in view of the disclosure of equivalence in the Paulet reference for reasons of economics or availability. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosures of the references for blackening/coloring.

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

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International application No.
PCT/US04/17786

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Claims 8-15 and 25 lack an inventive step under PCT Article 33(3) as being obvious over Lewis et al. (US 2554256) in view of Paulet (US 4018628). The Paulet reference is directed to formulations for blackening aluminum, as is the Lewis reference. The Paulet reference discloses ammonium molybdate or heptamolybdate (column 2, lines 4-7). It would have been obvious to the ordinary artisan to modify the formulations of the Lewis reference in view of the disclosure of equivalence in the Paulet reference for reasons of economics or availability. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosures of the references for blackening/coloring.

Claim 25 lacks an inventive step under PCT Article 33(3) as being obvious over Belkin et al. (SU 1678900 A1, as evidenced by USPTO obtained translation). Aluminum substrates are coated to provide corrosion protection, as required by claim 25. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosure of the reference for coating.

Claim 25 lacks an inventive step under PCT Article 33(3) as being obvious over Merekina et al. (SU 827613 B, as evidenced by USPTO obtained translation). Zinc substrates are coated to provide corrosion protection, as required by claim 25. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosure of the reference for coating.

Claims 1-25 satisfy the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

Claim 17 satisfies the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest further providing upon the coated substrates resulting from coating the zinc or aluminum substrate with the respective formulations a corrosion resistant coating of zinc and aluminum flakes in an inorganic binder.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Metal Coatings International Inc.
Int'l. App. No. : PCT/US04/17786
Int'l. Filing Date : 4 June 2004
Title : COMPOSITIONS AND METHODS FOR
DARKENING AND IMPARTING CORROSION-
RESISTANT PROPERTIES TO ZINC OR
OTHER ACTIVE METALS
Attorney Docket : MCII200002PCT

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

**RESPONSE TO INTERNATIONAL SEARCH REPORT
AND WRITTEN OPINION**

Dear Sir:

This is in response to the International Search Report and Written Opinion
mailed in the above application on October 13, 2004.

CERTIFICATE OF MAILING

I hereby certify that this Response and the documents referred to as being enclosed are being
directly transmitted via facsimile No. 011 41 22 740 1435 to WIPO on
Dec. 10, 2004 and also being couriered to WIPO, 34 chemin des
colombettes, 1211 Geneva 20, Switzerland via DHL on Dec. 10, 2004. A
copy is also being faxed to the U.S. Patent and Trademark Office (PCT) ISA/US No. (703)305-320
on Dec. 10, 2004.

By: Mary Ann Temesvari
Mary Ann Temesvari

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AP

Remarks

The Examiner cited a number of references which purportedly very closely show the claimed subject matter (designated by the "X" reference), and/or which show similarly related subject matter (shown by the "Y" designation). Numerous other references were cited which were given "A" designations, generally suggesting less relevance.

Specifically, the Examiner acknowledged that claims 1-25 met the requirements for industrial applicability. As for inventive step, the Examiner noted that claim 17 met this requirement, however, asserted that claims 8-15 and 25 allegedly did not. As for novelty, the Examiner indicated that claims 8-15, 17, and 25 were novel, however, contended that claims 1-7, 16, and 18-24, were not. Thus, one claim, claim 17, appears to meet all three requirements.

The Examiner also objected to claims 1-25 for allegedly lacking clarity because the claims are allegedly not fully supported by the description. Specifically, the Examiner alleged that the formulations are not described as to the basis upon which they are prepared, i.e. weight percent, volume percent, mole percent or otherwise.

These compositions and their percentages are expressed in weight percent. It is submitted that the Examiner's objections in this regard be withdrawn.

Concerning the requirements for patentability, the Examiner asserted that:

Claims 1-7 lack novelty under PCT Article 33(2) as being anticipated by Shipley, Jr., et al. (US 3650957). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate (column 4, line 74 to column 5, line 65; examples 12, 13, and 19). Concentrations are "about" 1:1 (claims 8-10) and 2.5 percent, as required by the claims.

Independent claim 1 has been amended to further distinguish the claimed compositions from the prior art. Claim 1 now expressly recites that the recited composition is "adapted for darkening and imparting corrosion-resistant properties" and that the composition "consists essentially of" the recited components. The Examiner will appreciate the significance of this terminology as it "excludes ingredients that materially affect the basic and novel characteristics of the claimed composition." *Atlas Powder Co. v. E.I. DuPont de Nemours & Co.*, 750 F.2d 1569, 224 USPQ 409 (Fed. Cir. 1984).

The '957 patent in contrast describes various copper etching solutions. Although several aqueous solutions are noted as containing ammonium chloride and ammonium molybdate (Examples 12, 13, and 19), these solutions also contain other ingredients that would affect the basic and novel characteristics of the claimed darkening and anti-corrosion compositions. For example, the solutions described in the '957 patent also contain cupric chloride dihydrate, tartaric acid, and ammonium nitrate. Simply put, the cupric etching solutions of the '957 patent are entirely different than the recited compositions of claims 1-7.

Furthermore, claim 1 has been amended to recite that the compositions are adapted for a specific "metallic surface selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof." The '957 patent in contrast is directed to etchants for cupreous metals.

Since independent claim 1 is believed to be patentable over the '957 patent, so, too, are claims 3-7 dependent therefrom.¹

Clearly, the claims at issue, as now amended, are patentable over the cited art.

The Examiner continued and asserted:

Claims 1-7, 16, 18-24 lack novelty under PCT Article 33(2) as being anticipated by Mitchell et al. (US 3314811). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate at "about" 1:1 by weight (column 3, lines 8-18), concentration determined at "about 1 ounce to about 3 pounds" per gallon of water (there are 8.34 pounds per gallon of water) (see claim 1) is "about" 2.5 percent, as required by claims 1-7. Such are for blackening aluminum substrates. Coated substrates with corrosion resistance are disclosed, as required by claims 16 and 18-24.

The claims at issue are patentable over the '811 patent. Claim 1, as now amended, recites in part that the composition "consists essentially of" the recited components. In contrast, the '811 patent describes compositions that must contain a metal salt (falling below aluminum in the electromotive series), and a sulfur-bearing compound. Claim 1 and claims 3-7 dependent therefrom, expressly exclude such additional ingredients.

Independent claim 16 and claims 19-24 dependent therefrom, are directed to coated metallic substrates. Claim 16 has been amended to parallel the amendments to claim 1 and so, is also patentable over the '811 patent for the

¹ Claim 2 has been cancelled in view of amendments to claim 1 (discussed herein) regarding ratios of ammonium chloride to ammonium molybdate.

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reasons set forth above. Since claim 16 is patentably distinguishable from the '811 patent, so, too, are claims 19-24 dependent therefrom.²

Furthermore, all claims at issue recite the metallic surface (either the substrate itself as in claim 16 or the composition adapted for application thereto as in claim 1) as "selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof." Aluminum is not included in this listing. And, claim 16 has been amended to expressly exclude aluminum. For at least these reasons, all claims at issue are patentable over the '811 patent.

The Examiner also argued:

Claims 1-7, 16, 18-24 lack novelty under PCT Article 33(2) as being anticipated by Lewis et al. (US 2554256). The reference discloses formulations of aqueous solutions of ammonium chloride and ammonium molybdate at "about" 1:1 by weight and concentration of "about" 2.5 percent (column 4, lines 15-18), as required by the claims. Such are for coloring aluminum substrates. Coated aluminum substrates with corrosion resistance are disclosed (column 3, lines 52-55), as required by claims 16 and 18-24.

As previously explained, independent claims 1 and 16 have been amended to expressly recite that the metallic surface is "selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof." Aluminum is not included in this listing. In contrast, the '256 patent is strictly limited to treatment of aluminum surfaces. For at least these reasons, independent claims 1 and 16 and claims 3-7 and 19-24 dependent therefrom, are all patentable over the '256 patent.

Next, the Examiner contended:

Claims 1-7, 16, and 18-24 lack novelty under PCT Article 33(2) as being anticipated by Eelkin et al. (SU 1678900 AI, as evidenced by USPTO obtained translation). The reference discloses aqueous formulations of ammonium chloride and ammonium molybdate at "about" 1:1 and "about" 2.5 percent, as required by claims 1-7. Aluminum substrates are coated to provide corrosion protection, as required by claims 16 and 18-24.

The SU '900 document fails to anticipate the cited claims. As previously noted, independent claims 1 and 16 have been amended to exclude ingredients that would affect the basic and novel characteristics of the recited compositions. In contrast, the SU '900 document discloses a solution containing an ammonium

² Claim 18 has been canceled in view of amendments to claim 16.

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or alkali metal phosphate, and ammonium or alkaline metal citrate. These ingredients are expressly excluded by the claims at issue.

Furthermore, all claims at issue are directed to metallic surfaces "selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof." Aluminum is not included in this group and was cancelled from the former listing in claim 16. The SU '900 document is strictly limited to aluminum. For at least these reasons, the claims at issue are patentable over the SU '900 document.

The Examiner further argued:

Claims 1-7, 16, and 18-24 lack novelty under PCT Article 33(2) as being anticipated by Merekina et al. (SU 827613 B, as evidenced by USPTO obtained translation). The reference discloses aqueous formulations of ammonium chloride and ammonium molybdate at "about" 1:1 and "about" 2.5 percent, as required by claims 1-7. Zinc substrates are coated to provide corrosion protection, as required by claims 16 and 18-24.

The SU '613 document fails to anticipate the claims at issue. Both independent claims 1 and 16 have been amended to recite that the ratio of ammonium chloride to ammonium molybdate is from about 1:2 to about 2:1. In contrast, the SU '613 document discloses the use of ammonium chloride in significantly greater proportions. For at least this reason, the claims at issue are patentable over the SU '613 document.

The Examiner further argued:

Claims 8-15 lack an inventive step under PCT Article 33(3) as being obvious over Shipley, Jr., et al. (US 3650957). The reference discloses that the source of the complexing molybdenum compound is not critical (column 5, lines 15-18). Thus, it would have been obvious to the ordinary artisan to employ any commercially available molybdate, such as heptamolybdate.

Independent claim 8 has been amended to specifically recite that the composition is "adapted for application to a metallic surface selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof." In sharp distinction, the '957 patent teaches that its compositions are for cupreous metals. The '957 patent entirely fails to teach or even suggest applying solutions to the specific metallic surfaces recited in claim 8. Since claim 8 is patentable over the '957 patent, so, too, are claims 9-15 dependent therefrom.

The Examiner further contended:

Claims 8-15 and 25 lack an inventive step under PCT Article 33(3) as being obvious over Mitchell et al. (US 3314811) in view of Paulet (US 4018628). The Paulet reference is directed to

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formulations for blackening aluminum, as is the Mitchell reference. The Paulet reference discloses ammonium molybdate or heptamolybdate (column 2, lines 4-7). It would have been obvious to the ordinary artisan to modify the formulations of the Mitchell reference in view of the disclosure of equivalence in the Paulet reference for reasons of economics or availability. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosures of the references for blackening/coloring.

As previously explained, the '811 patent is not particularly relevant. The '811 patent is directed to compositions for treating aluminum. Independent claim 8 has been amended to recite a specific listing of metallic surfaces, which does not include aluminum. For at least this reason, claims 8 and 9-15 dependent therefrom are patentable over the cited patents.

Claim 25 depends from independent claim 16 which has also been amended to exclude aluminum as the metallic substrate to which a darkening coating is applied. Claim 25 recites that the darkening coating is disposed on a corrosion-resistant coating that comprises zinc flakes and aluminum flakes. The '811 patent fails to teach application of its coatings to such a flake-containing composition. Specifically, claim 25 recites a specific coated substrate having a coating comprising zinc flakes and aluminum flakes, that is disposed between (i) a metal substrate selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, and (ii) a darkening coating consisting essentially of the components recited in claim 16, as now amended, from which claim 25 depends. In no way does the '811 patent teach, suggest, or even hint at this particular array of coatings on a certain substrate. For at least these reasons, claim 25 is patentable over the cited art. For at least these reasons, all of claims 8-15 and 25 are patentable over the cited art.

The '628 patent fails to remedy the deficiencies of the '811 patent. The '628 patent is also strictly limited to the treatment of aluminum.

Neither of the cited patents teaches or even suggests an aqueous composition adapted for application to a metallic substrate selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof. For at least these reasons, all of claims 8-15 and 25 are patentable.

The Examiner continued and argued:

Claims 8-15 and 25 lack an inventive step under PCT Article 33(3) as being obvious over Lewis et al. (US 2554256) in view of Paulet (US 4018628). The Paulet reference is directed to

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formulations for blackening aluminum, as is the Lewis reference. The Paulet reference discloses ammonium molybdate or heptamolybdate (column 2, lines 4-7). It would have been obvious to the ordinary artisan to modify the formulations of the Lewis reference in view of the disclosure of equivalence in the Paulet reference for reasons of economics or availability. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosures of the references for blackening/coloring.

As previously noted, independent claim 8 has been amended to recite that its compositions are adapted for application to particular metallic surfaces, i.e. "zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof." Aluminum is not included. Both the '256 patent and the '628 patent are directed to the treatment of aluminum. For at least this reason, they fail to teach or even suggest the subject matter of claims 8-15.

Claim 25 recites a specific coated substrate having a coating comprising zinc flakes and aluminum flakes, that is disposed between (i) a metal substrate selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, and (ii) a darkening coating consisting essentially of the components recited in claim 16, as now amended, from which claim 25 depends. In no way do the '256 patent and/or the '628 patent teach, suggest, or even hint at this particular array of coatings on a certain substrate. For at least these reasons, claim 25 is patentable over the cited art.

The Examiner further contended:

Claim 25 lacks an inventive step under PCT Article 33(3) as being obvious over Belkin et al. (SU 1678900 A1, as evidenced by USPTO obtained translation). Aluminum substrates are coated to provide corrosion protection, as required by claim 25. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosure of the reference for coating.

Claim 25 recites a specific coated substrate having a coating comprising zinc flakes and aluminum flakes, that is disposed between (i) a metal substrate selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, and (ii) a darkening coating consisting essentially of the components recited in claim 16, as now amended, from which claim 25 depends. In no way does the SU '613 document teach, suggest, or even hint at this particular array of coatings on a certain substrate. For at least these reasons, claim 25 is patentable over the cited art.

The Examiner further contended:

Claim 25 lacks an inventive step under PCT Article 33(3) as being

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obvious over Merekina et al. (SU 827613 B, as evidenced by USPTO obtained translation). Zinc substrates are coated to provide corrosion protection, as required by claim 25. The substrate of claim 25 is merely another aluminum substrate suitable to the disclosure of the reference for coating.

Claim 25 recites a specific coated substrate having a coating comprising zinc flakes and aluminum flakes, that is disposed between (i) a metal substrate selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, and (ii) a darkening coating consisting essentially of the components recited in claim 16, 'as now amended, from which claim 25 depends. In no way does the SU '900 document teach, suggest, or even hint at this particular array of coatings on a certain substrate. Furthermore, claim 16 from which claim 25 depends, was amended to recite that the darkening coating composition contains a particular proportion of ammonium chloride to ammonium molybdate. The SU '613 document entirely fails to teach that particular range of proportions. For at least these reasons, claim 25 is patentable over the cited art.

The Examiner continued and stated:

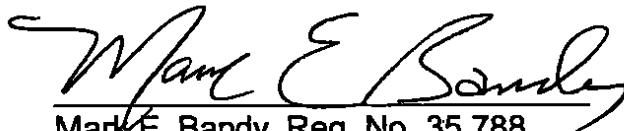
Claims 1-25 satisfy the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

Claim 17 satisfies the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest further providing upon the coated substrates resulting from coating the zinc or aluminum substrate with the respective formulations a corrosion resistant coating of zinc and aluminum flakes in an inorganic binder.

In view of the foregoing, it is respectfully submitted that all claims 1, 3-17, and 19-25 are patentable over the cited art.

Respectfully submitted,

Dec 10, 2004
Date


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(216) 861-5582

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We claim:

1. A composition adapted for darkening and imparting corrosion-resistant properties to a metallic surface selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, the composition
5 consisting essentially of:
from about 0.1 percent to about 5 percent ammonium chloride;
from about 0.1 percent to about 5 percent ammonium molybdate;
and
from about 90 percent to about 99.8 percent water;
10 wherein the ratio of ammonium chloride to ammonium molybdate is
from about 1:2 to about 2:1.
2. (Canceled)
- 15 3. The composition of claim 1 wherein said ratio is about 1:1.
4. The composition of claim 1 wherein the concentration of ammonium chloride is from about 0.5 percent to about 3 percent.
- 20 5. The composition of claim 1 wherein the concentration of ammonium chloride is about 2.5 percent.
6. The composition of claim 1 wherein the concentration of ammonium molybdate is from about 0.5 percent to about 3 percent.
- 25 7. The composition of claim 1 wherein the concentration of ammonium molybdate is about 2.5 percent.
8. An aqueous composition adapted for application to a metallic
30 surface selected from zinc, magnesium, manganese, and alloys and intermetallic mixtures thereof, the composition comprising:
from about 0.1 percent to about 5 percent ammonium chloride; and

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from about 0.1 percent to about 5 percent ammonium
heptamolybdate;

wherein the ratio of ammonium chloride to ammonium
heptamolybdate is from about 1:3 to about 3:1.

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9. The composition of claim 8 wherein said ratio is from about 1:2 to
about 2:1.

10. The composition of claim 8 wherein said ratio is about 1:1.

10

11. The composition of claim 8 wherein the concentration of ammonium
chloride is from about 0.5 percent to about 3 percent.

12. The composition of claim 10 wherein the concentration of
15 ammonium chloride is about 2.5 percent.

13. The composition of claim 8 wherein the concentration of ammonium
heptamolybdate is from about 0.5 percent to about 3 percent.

20 14. The composition of claim 10 wherein the concentration of
ammonium heptamolybdate is about 2.5 percent.

15. The composition of claim 10 comprising about 2.5 percent
ammonium chloride and about 2.5 percent ammonium heptamolybdate.

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16. A coated metallic substrate comprising:

a metal substrate having an outer surface, wherein said metal is
selected from the group consisting of zinc, magnesium, manganese, and alloys
and intermetallic mixtures thereof; and

30 a darkening coating disposed on said substrate, said coating
formed from an aqueous composition consisting essentially of (i) from about 0.1
percent to about 5 percent ammonium chloride, and (ii) from about 0.1 percent to

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about 5 percent ammonium molybdate, wherein the ratio of ammonium chloride to ammonium molybdate is from about 1:2 to about 2:1.

5 17. The coated substrate of claim 16 further comprising:
 a corrosion-resistant coating disposed on said darkening coating,
wherein said corrosion-resistant coating comprises zinc flakes and aluminum
flakes dispersed in an inorganic binder.

10 18. (Canceled)

 19. The coated substrate of claim 16 wherein said ratio is about 1:1.

 20. The coated substrate of claim 16 wherein the concentration of
ammonium chloride is from about 0.5 percent to about 3 percent.

15 21. The coated substrate of claim 16 wherein the concentration of
ammonium chloride is about 2.5 percent.

 22. The coated substrate of claim 16 wherein the concentration of
20 ammonium molybdate is from about 0.5 percent to about 3 percent.

 23. The coated substrate of claim 16 wherein the concentration of
ammonium molybdate is about 2.5 percent.

25 24. The coated substrate of claim 16 wherein the concentration of
ammonium chloride is about 2.5 percent and the concentration of ammonium
molybdate is about 2.5 percent.

 25. The coated substrate of claim 16 further comprising;
30 a corrosion-resistant coating disposed between said outer surface
of said metal substrate and said darkening coating, wherein said corrosion-
resistant coating comprises zinc flakes and aluminum flakes dispersed in an
organic binder.

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26. A method for darkening the surface of zinc comprising:
providing a substrate having an outer surface of zinc;
providing a composition including from about 0.1 percent to about 5
5 percent ammonium chloride and from about 0.1 percent to about 5 percent
ammonium molybdate; and
applying said composition to said outer surface of said zinc to form
a darkening coating thereon.

10 27. The method of claim 26 further comprising, after said step of
applying said composition, a step of:
drying said coating at a temperature of from about 37°C (100°F) to
about 121°C (250°F).

15 28. The method of claim 26 further comprising, after said step of
applying said composition, a step of:
exposing said coating to a curing operation.

29. The method of claim 26 wherein said composition comprises from
20 about 0.5 percent to about 3 percent ammonium chloride and from about 0.5
percent to about 3 percent ammonium molybdate.

30. The method of claim 26 wherein said composition comprises about
2.5 percent ammonium chloride and about 2.5 percent ammonium molybdate.

25 31. A method for imparting corrosion inhibiting properties to a substrate
of an active metal, said method comprising:
providing a substrate of an active metal;
providing a composition including from about 0.1 percent to about 5
30 percent ammonium chloride and from about 0.1 percent to about 5 percent
ammonium molybdate, wherein the ratio of ammonium chloride to ammonium
molybdate is from about 1:3 to about 3:1; and
applying said composition to said substrate.

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32. The method of claim 31 further comprising, after said step of applying said composition, a step of:
drying said coating at a temperature of from about 37°C (100°F) to
5 about 121°C (250°F).

33. The method of claim 31 further comprising, after said step of applying said composition, a step of:
exposing said coating to a curing operation.

34. The method of claim 31 wherein said composition comprises from about 0.5 percent to about 3 percent ammonium chloride and from about 0.5 percent to about 3 percent ammonium molybdate.

35. The method of claim 31 wherein said composition comprises about 2.5 percent ammonium chloride and about 2.5 percent ammonium molybdate.

36. A method for imparting corrosion resistance properties to a zinc surface, said method comprising:
providing a component having an outer surface of zinc;
providing a composition including from about 0.1 percent to about 5 percent ammonium chloride and from about 0.1 percent to about 5 percent ammonium molybdate; and
applying said composition to said outer surface of said zinc.

Expediente No		05123300	No de Folio
Item		No de unidades	✓
1	CD		
2	DVD		
3	REVISTA		
4	LIBRO		
5	PERIODICO		
6	DISQUETES		
7	SOBRE DE MANILA	1	
8	SOBRE BLANCO TAMAÑO CARTA		
9	SOBRE BLANCO TAMAÑO OFICIO		
10	OTROS.		

Observaciones:

Contiene 2 figura

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SUPERINDUSTRIA Y COMERCIO
Radicacon : 05123300 00000000 Folios: 226
Fecha (AMD): 2005-12-05 16:56:25
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION <i>PCT</i> MODELO DE UTILIDAD	()	()
- Indicación de que se solicita la concesión de una patente.	()	()
- Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	()
- Descripción de la invención.	()	()
- Dibujos de ser estos pertinentes.	()	()
- Comprobante de Pago de las tasas establecidas.	()	()

COMPLETA <i>X</i>	INCOMPLETA ()
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DISEÑO INDUSTRIAL ()	
- Indicación de que se solicita el registro de Diseño Industrial	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()
- Representación gráfica o fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño.	()
- Comprobante de pago de las tasas establecidas	()

COMPLETA ()	INCOMPLETA ()
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ESQUEMA DE TRAZADO ()	
- Indicación de que solicita el registro de un Esquema de trazado.	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()
- Representación gráfica del esquema de trazado	()
- Comprobante de pago de las tasas establecidas	()

COMPLETA ()	INCOMPLETA ()
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Firma Responsable:

Fecha:

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
RODRIGUEZ D'ALEMAN DILIA MARIA
Apoderado(a) y/o Representante de
METAL COATINGS INTERNATIONAL INC.

REFERENCIA Radicación No. 5 123300
Solicitud internacional US2004/017786
Fecha inicio fase nacional 05/01/2006
Trámite 11
Evento 379
Actuación 430 784
Oficio No.

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

1. La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486.

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

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

ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la división de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de
fecha 27-ENE-2006
adpa11