

SUPERINDUSTRIA Y COMERCIO
 Radicacion : 00093193 00000004 Folios: 2
 Fecha (AMD): 2003-02-14 09:00:10
 Trámite : 000 PATENTES 0 1 REGISTRO/ 530 PETICION
 Dependencia: 2500 DIVISION DE NUEVAS CREACIONES

SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
MINISTERIO DE DESARROLLO ECONOMICO

REF: EXPEDIENTE : 00093193
SOLICITANTE: MBT HOLDING AG
FECHA DE LA SOLICITUD: DICIEMBRE 6, 2000
TITULO: PROCEDIMIENTO DE PREPARACION DE UN ACELERADOR
PARA HORMIGON

ASUNTO: SOLICITUD ESTUDIO DE FONDO

DILIA RODRÍGUEZ D'ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted que habiéndose surtido la publicación de la presente solicitud, en la Gaceta de la Propiedad Industrial N°.520 de fecha Septiembre 27 de 2002 se proceda con el estudio de Fondo.

Para tal fin me permito anexar la tasa correspondiente.

Agradezco continuar con el presente trámite.

Señor Jefe,


DILIA RODRÍGUEZ D'ALEMAN
T.P.No. 20824 del CSJ

P-388

SUPERINDUSTRIA Y COMERCIO
Radicacion : 000933193 00000004 Folios: 2
Fecha (AMD): 2003-02-14 09:30:10
Tramite : DAE PATENTES D 1 REGISTRO/ 530 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 03 - 7,986
FECHA : FEBRERO 7 DE 2003

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE NODET Y CO. COLOMBIA	CONSIGNACION	BANCO POPULAR	050-00110-6	9018618	06/02/2003	3,258,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		85 EXAMEN DE PATENTABILIDAD DE INVEN	335,000.
		TOTAL :	\$ 335,000.00

SON: TRESCIENTOS TREINTA Y CINCO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

69

A 388

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 30 de Agosto de 2005

Doctora

DILIA RODRIGUEZ D'ALEMAN

Representante **MBT HOLDING AG**

ASUNTO

Radicación No. **00-93193**

Trámite **002**

Evento **001**

Actuación **430**

Oficio

Folios **051**

7979

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

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 20 a 26 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 10 reivindicaciones en los folios 227 a 28 de la solicitud en estudio.
- c) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 6 de diciembre de 2000, y en el momento de la radicación **SI** se reclamo prioridad de la primera solicitud presentada en Gran Bretaña GB 9928977.9.

2) Objeto de la invención

- a) Las reivindicaciones 1 a 10 de la solicitud en estudio se refieren a un procedimiento de prelación de un acelerador para hormigón proyectado caracterizado porque comprende esencialmente las etapas de (i) disolver sulfato de aluminio e hidróxido de aluminio en agua que opcionalmente contiene una amina disuelta en la misma, y (ii) opcionalmente añadir uno de por lo menos un estabilizante y por lo menos un agente desespumante; siendo tales las proporciones de los ingredientes presentes que el producto final contiene de 3 a 12% en peso de sulfato de aluminio (medido como Al_2O_3) hasta 30% en peso de hidróxido de aluminio amorfo hasta 15% en amina, hasta 3% en agente desespumante y hasta 0,06 moles/kg de estabilizante, siendo seleccionado el estabilizante entre ácidos hidroxicarboxílicos, ácidos fosfóricos y sales no alcalinas de ácidos fosfóricos.

- b) El anterior procedimiento busca fabricar un acelerante para hormigón.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 04 B 22/00

3) Claridad de la Solicitud

- a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones establece

"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

La descripción afirma que el proceso radica en disolver en agua sulfato de aluminio y también hidróxido de aluminio. Además afirma todos los hidróxidos de aluminio proporcionan resultados satisfactorios. Cualquier técnico medio sabe que el hidróxido de aluminio es totalmente insoluble en agua. Ni en agua fría ni en agua caliente. Por lo tanto, no es procedente que basen toda una solicitud en una imposibilidad fisicoquímica. Debe el solicitante explicar esta incongruencia.

- b) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro toda vez que:

- i) No tiene sustento técnico. El capítulo reivindicatorio se basa en que el hidróxido de aluminio se disuelve en agua. Cualquier técnico medio sabe que el hidróxido de aluminio es totalmente insoluble en agua. Ni en agua fría ni en agua caliente. Por lo tanto, no es procedente que basen toda una solicitud en una imposibilidad fisicoquímica.
- ii) No es claro el procedimiento que quieren proteger. De acuerdo a lo allí contemplado el único proceso que se pretende proteger es disolver. Y disolver es obvio para cualquier persona que entienda del arte. Otra cosa es que fisicoquímicamente tenga imposibilidades como se discutió antes. Sin embargo, el procedimiento de disolver resulta evidente.
- iii) La reivindicación 10 no es clara en su presentación. Debe revisarse.

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

“El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.”

“Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40.”

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 04 B 22/00 y las más cercanas a ellas, se encontró que antes del 8 de diciembre de 1999 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con soluciones o mezclas de compuestos de aluminio que pueden ser empleados como acelerantes para hormigón

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	EP 0 946 451	Solidifying and hardening accelerator fro hydraulic binders	1998.05.07
D2	EP 0 775 097	Cement accelerating admixture	1996.02.22
D3	Nouveau traité de chimie minérale Tome VI	Sulfates d'aluminium basiques	1961
D4	US 4 976 316	Method of accelerating set of cement by wash over fluid containing alkanolamine	1990.12.11
D5	US 4 284 611	Aqueous phosphate stabilized polyaluminium sulfate solutions and preparation thereof	1981.08.18
D6	GB 1 210 549	Production of edible tubular collagen casing	1970.10.28
D7	FICHAS INTERNACIONALES DE SEGURIDAD QUÍMICA	Sulfato de aluminio	1994
D8	FICHAS INTERNACIONALES DE SEGURIDAD QUÍMICA	Hidróxido de aluminio	1994

5) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación de la novedad en referencia a un nuevo uso

El art. 21 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los productos o procedimiento ya patentados, comprendidos en el estado de la técnica, no serán objeto de nueva patente, por el simple hecho de atribuirse un uso distinto al originalmente comprendido por la patente inicial."

De acuerdo a lo observado en toda la solicitud, el procedimiento objeto de la solicitud se reduce a disolver sulfato de aluminio e hidróxido de aluminio en agua. El resto de ingredientes son opcionales. Si se observa el documento D7 se encuentra que es ampliamente conocido el disolver el sulfato de aluminio en agua, tanto que ya posee una ficha técnica al respecto. Es decir, no se le puede otorgar protección por el solo hecho de disolver. Como ya se cuestionó en líneas anteriores, el documento D8 revela que no es posible disolver el hidróxido de aluminio. Esto no implica que no se haya intentado. Si se ha hecho, y por lo mismo se puede sacar una ficha técnica internacional donde se afirma categóricamente que dicha disolución es fisicoquímicamente imposible. En contacto prolongado con el agua el hidróxido forma geles, no una solución. Sin embargo, y de acuerdo con D7 y D8 es claro que es ampliamente conocido en la técnica el combinar el sulfato de aluminio con el agua y el hidróxido de aluminio con el agua.

D3 revela las mezclas de sulfato de aluminio en solución junto con el hidrogel de alumina para obtener un compuesto como el que se quiere proteger en la presente solicitud. Es decir, independientemente del uso que se le quiera dar a la mezcla, esta ya existía mucho tiempo antes de la solicitud colombiana.

D6 también muestra este tipo de mezclas.

Por lo mismo, no se le podría otorgar una nueva patente a algo que ya se ha trabajado durante mucho tiempo, y que podría variar solo en el uso que se le va a dar. Resulta demasiado evidente, en consecuencia, para un técnico medio obtener lo que quiere proteger el solicitante para Colombia partiendo de estos documentos

b) Evaluación del Nivel Inventivo

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

D1 contempla un acelerador para cementos hidráulicos que contiene varios componentes:

- sales de aluminio básico y/o hidróxido de aluminio (primer componente básico de la solicitud colombiana)
- sulfato de aluminio y/o ácido sulfúrico (segundo componente básico de la solicitud colombiana)
- ácidos carboxílicos orgánicos o mezclas de al menos dos de esos ácidos carboxílicos (primer componente opcional de la solicitud colombiana)
- sales de aluminio de los ácidos carboxílicos orgánicos y otros componentes.

Los compuestos básicos de la solicitud colombiana, sulfato de aluminio e hidróxido de aluminio, los revela D1. Los demás componentes que son opcionales para la solicitud colombiana, los revela en su mayoría D1. Algunos pocos (muy pocos) componentes que no se revelan en D1, resultan evidentes para una persona versada en la materia, toda vez que cumplen con la función esperada. De lo anterior, resultaría demasiado evidente para una persona que conozca del arte llegar a lo que se quiere proteger acá en Colombia partiendo de D1.

D2 revela mezclas de hidroxisulfato de aluminio e hidróxido de aluminio junto con aminas. También incorporan ácidos. Es muy similar la materia de los dos documentos. Por lo mismo, resulta demasiado evidente llegar a lo que quiere proteger el solicitante partiendo de D2.

D4 muestra el uso de aminas como elemento importante para acelerar el fraguado de cementos. Este documento soporta lo encontrado en D1 y D2.

D5 muestra combinaciones de fosfatos con polímeros de sulfatos y aluminio. Inicialmente se hace reaccionar el hidrato de aluminio con ácido fosfórico y luego con soluciones de sulfato de aluminio. Básicamente lo mismo que se pretende proteger en la presente solicitud, aunque congruente técnicamente.

c) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	EP 0 946 451	1 - 10	Nivel inventivo
D2	EP 0 775 097	1 - 10	Nivel inventivo
D3	Nouveau traité de chimie minérale Tome VI	1 - 10	Novedad
			Nivel inventivo
D4	US 4 976 316	1 - 10	Nivel inventivo
D5	US 4 284 611	1 - 10	Nivel inventivo
D6	GB 1 210 549	1 - 10	Novedad
			Nivel inventivo
D7	FICHAS INTERNACIONALES DE SEGURIDAD QUÍMICA	1 - 10	Novedad
			Nivel inventivo
D8	FICHAS INTERNACIONALES DE SEGURIDAD QUÍMICA	1 - 10	Novedad
			Nivel inventivo

6) Notificación

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

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha

08 SET. 2005

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
1306	202003	

D1

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 946 451 B1

(12)

EUROPÄISCHE PATENTSCHRIFT

(45) Veröffentlichungstag und Bekanntmachung des Hinweises auf die Patenterteilung:
20.09.2000 Patentblatt 2000/38

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C04B 24/04, C04B 24/16

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(54) ERSTARRUNGS- UND ERHÄRTUNGSBESCHLEUNIGER FÜR HYDRAULISCHE BINDEMittel
SOLIDIFYING AND HARDENING ACCELERATOR FOR HYDRAULIC BINDERS
ACCELERATEUR DE SOLIDIFICATION ET DE PRISE POUR LIANTS HYDRAULIQUES

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(43) Veröffentlichungstag der Anmeldung:
08.10.1999 Patentblatt 1999/40

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(56) Entgegenhaltungen:
EP-A- 0 667 388 EP-A- 0 670 292
WO-A-95/03267 DE-A- 3 233 474

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94-083589 XP002033948 & ZA 9 305 848 A (HM
LICENCE CO PTY LTD), 29. Dezember 1993

EP 0 946 451 B1

Anmerkung: Innerhalb von neun Monaten nach der Bekanntmachung des Hinweises auf die Erteilung des europäischen Patents kann jedermann beim Europäischen Patentamt gegen das erteilte europäische Patent Einspruch einlegen. Der Einspruch ist schriftlich einzureichen und zu begründen. Er gilt erst als eingelegt, wenn die Einspruchsgebühr entrichtet worden ist. (Art. 99(1) Europäisches Patentübereinkommen).

EP 0 946 451 B1

Beschreibung

[0001] Gegenstand der vorliegenden Erfindung sind stabile Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel in gelöster Form, sowie deren Herstellung und Verwendung

[0002] Aus der EP 0 76 927 B1 ist ein alkalfreier Abbindebeschleuniger auf der Basis von Aluminiumhydroxyd bekannt. Die weiteren Bestandteile dieses Mittels sind gemäß Anspruch 1 wenigstens ein wasserlösliches Sulfat und/oder Nitrat und/oder Formiat der Erdalkali und Übergangsmetalle, die dem Hauptbestandteil durch einfaches Zumischen zugegeben werden. Aus Seite 2, Zeile 55 geht auch eindeutig hervor, daß es sich bei diesem Mittel um eine pulverförmige Mischung handelt, die dem hydraulischen Bindemittel in fester Form zugegeben wird.

Lediglich um eine übermäßige Staubeentwicklung zu vermeiden, werden dem Gemisch wasserlösliche Verbindungen zugegeben.

[0003] In der DD 286 344 A1 werden kationische Aluminiumsalze, erhalten durch die Umsetzung eines gefällten Aluminiumhydroxyds mit konzentrierter Ameisensäure, Essig- oder Salpetersäure, beschrieben, die zum entsprechenden hydraulischen abbindendem Zement oder Mörtel in Form eines Pulvers zugemischt werden. Die durch die Umsetzung des Aluminiumhydroxyds mit den entsprechenden Säuren entstehenden Verbindungen lassen sich durch eine allgemeine Formel beschreiben, z.B. $Al(OH)_3 \cdot R \cdot x H_2O$, $Al(OH)_3 \cdot R_2 \cdot x H_2O$ oder $AlR_3 \cdot x H_2O$. Diese Aluminiumsalze enthalten keine Sulfat und Chloridionen.

[0004] In der FR-2.471.955 wird ein Verfahren zur beschleunigten Abbinde von Zement beschrieben, das dadurch gekennzeichnet ist, daß als beschleunigendes Agens Blausäure-Formaldehyd, Calciumformiat und Calciumnitrat in Form einer Lösung verwendet wird, z.B. siehe Seite 3, ab Zeilen 18, Beispiele.

[0005] Schließlich wurde in der EP 0 657 388 A1 ebenfalls ein Verfahren zur Abbindebeschleunigung von hydraulischen Bindemitteln bekanntgemacht, das dadurch charakterisiert ist, daß das beschleunigende Agens eine Mischung ist, die mindestens ein wasserlösliches Sulfat eines mehrwertigen Kations, insbesondere des Aluminiums und eine weitere wasserlösliche Komponente, z.B. Calciumsulfat, Calciumnitrat, basisches Aluminiumsulfat und noch mindestens eine weitere Komponente enthält. Diese weitere Komponente kann gemäß Anspruch 24 ein Dispergiermittel, ein anorganisches Bindemittel, ein Verflüssiger oder ein Entlüftungsmittel sein.

Der Abbindebeschleuniger soll auch in Form einer wässrigen Dispersion angewendet werden können.

Abbindebeschleuniger sind besonders interessant für die Praxis, wenn sie in flüssiger Form verwendbar sind.

Gegenüber den festen Beschleunigern ist im wesentlichen ihre bessere Dosierbarkeit, die schnellere Freigabe der Wirksubstanz(en) und natürlich die vernachlässigbare Staub- bzw. Aerosolentwicklung bei der Handhabung hervorzuheben.

Die klassischen flüssigen, alkalischen Beschleuniger, z.B. Natriumaluminat und Wasserglas wirken nicht nur wegen ihres hohen pH-Wertes ätzend, sondern führen auch durch den hohen Alkalimetallgehalt in den Beton zu z.T. massiven Abfall der Endfestigkeit.

[0006] Neuere, flüssige Beschleuniger bestehen hauptsächlich aus wässrigen Suspensionen von basischen Aluminiumsulfaten. Sie sind jedoch, im allgemeinen nicht froststabil, neigen zur Sedimentation und zeigen, obwohl sie in flüssiger Form beim Naßspritzverfahren anwendbar wären, eine ungenügende Frühfestigkeitsentwicklung und wirken auch je nach Zementtyp nur noch schwach beschleunigend.

Außerdem sind im Handel befindliche konzentrierte Aluminiumsalzlösungen z.B. $Al_2(SO_4)_3$ mit ca. 8 % Al_2O_3 oder Aluminiumnitratlösungen mit ca. 5 % Al_2O_3 sind zumindest für das Naßspritzverfahren nicht geeignet, da sie wegen des erhöhten Wassereintrags in die Betonmasse und des damit verbundenen erhöhten Wasser-Zement-Faktors eine unerwünschte niedrige Druckfestigkeit bedingen.

[0007] Der vorliegenden Erfindung lag daher die Aufgabe zugrunde, einen konzentrierten, in Wasser gelösten Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel zur Verfügung zu stellen, der nicht die Nachteile der klassischen flüssigen Beschleuniger, wie Natriumaluminat bzw. Wasserglas besitzt und sich vor allem für das Naßspritzverfahren gut eignet.

[0008] Die Aufgabe konnte überraschenderweise durch neue flüssige Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel wie Zement gelöst werden, die durch ein Verfahren erhältlich sind, das dadurch gekennzeichnet ist, daß folgende Komponenten

Komponente a: basische Aluminiumsalze und/oder Aluminiumhydroxyd

Komponente b: Aluminiumsulfat und/oder Schwefelsäure

Komponente c: organische Carbonsäuren oder Mischungen zumindest zweier der organischen Carbonsäuren

Komponente d: Aluminiumsalze der organischen Carbonsäuren

Komponente e: organische und/oder anorganische Sulfate und/oder Hydrogensulfate und/oder Carbonate und/oder Hydrogencarbonate und/oder Erdalkalioxyde und/oder Erdalkalihydroxyde bei Temperaturen bis 150 °C in Wasser zur Reaktion gebracht werden, so daß dabei eine Lösung erhalten wird, wobei

1. alle Komponenten oder eine Auswahl der Komponenten miteinander reagieren, so daß die Molverhältnisse des Aluminiums zu Sulfat im Endprodukt 0,83 bis 13,3 und die Molverhältnisse des Aluminiums zur organischen Carbonsäure 0,67 bis 33,3 betragen oder

2. alle Komponenten außer Komponente e oder eine Auswahl der Komponenten außer Komponente e miteinander reagieren, so daß die Molverhältnisse des Aluminiums zu Sulfat im Endprodukt 0,83 bis 13,3 und die Molverhältnisse des Aluminiums zur organischen Carbonsäure im Endprodukt 0,67 bis 33,3 betragen oder

3. die Komponente e nachträglich im Reaktionsprodukt nach Punkt 2. aufgelöst wird.

Als basische Aluminiumsalze werden bevorzugt die basischen Sulfate, Carbonate, Carbonatsulfate und Nitrate und Mischungen von mindestens zwei dieser Komponenten eingesetzt.

Als organische Carbonsäuren kommen im wesentlichen die Monocarbonsäuren Hydroxycarbonsäuren und Dicarbonsäuren, z.B. Ameisensäure, Essigsäure, Glycolsäure, Milchsäure und deren Mischungen in Betracht.

Als anorganische und organische Sulfate bzw. Hydrogensulfate werden die Erdsulfate und/oder Triethanolaminsalze und/oder Diethanolaminsalze der Schwefelsäure verwendet. Aber auch die Alkalisalze der Schwefelsäure kommen als Sulfat oder Hydrogensulfat zur Verwendung.

Als Carbonate und/oder Hydrogencarbonate können die Erdsulfate verwendet werden. Weiterhin ist es möglich, auch Erdsulfate oder Erdsulfathydroxyde anzuwenden.

Die erfindungsgemäßen Abbindebeschleuniger können je nach Bedarf zusammen mit anderen Verbindungen wie z.B. Abbindeverzögerern, Verflüssigern und Rückprallvermindernern eingesetzt werden.

Die folgenden Beispiele beleuchten den Erfindungsgegenstand näher ohne diesen zu beschränken:

Herstellungsbispiele:

Beispiel 1

[0008] 675 g basisches Aluminiumcarbonat (17,77 % Al_2O_3) wurden in 80 g Ameisensäure 85 %ig aufgeschlämmt und mit 324 g Aluminiumsulfat (17,5 % Al_2O_3) versetzt. Unter Rühren wurde bei einer Temperatur von 50 bis 60 °C nach 1,5 Stunden eine fast klare Lösung erhalten. Die Lösung ist über einen Zeitraum von mehr als 3 Monaten stabil.

Beispiel 2

[0010] 490 g basisches Aluminiumsulfat (16,7 % Al_2O_3) wurden in 38,9 g Milchsäure 80 %ig aufgeschlämmt und mit 375 g Aluminiumsulfat (17,5 % Al_2O_3) versetzt. Unter Rühren wurde bei einer Temperatur von 51 bis 72 °C nach 1,5 Stunden eine leicht trübe Lösung erhalten.

Beispiel 3

[0011] 500 g basisches Aluminiumsulfat (17,8 % Al_2O_3) wurden mit 76 g Oxalsäure-Dihydrat und mit 375 g Aluminiumsulfat (17,5 % Al_2O_3) versetzt. Unter Rühren wurde bei einer Temperatur von 75 °C nach 1 Stunde eine klare Lösung erhalten. Die Lösung wurde auf ein Gewicht von 848,6 g aufkonzentriert.

Beispiel 4

[0012] 101 kg basisches Aluminiumcarbonat (19,15 % Al_2O_3) wurden in 8,2 kg Wasser und 15,2 kg Ameisensäure 85 %ig aufgeschlämmt und mit 72 kg Aluminiumsulfat (17,5 % Al_2O_3) versetzt. Unter Rühren wurde bei einer Temperatur von 35 bis 80 °C nach 3 Stunden eine fast klare Lösung erhalten. Die Lösung ist über einen Zeitraum von mehr als 3 Monaten stabil.

Beispiel 5

[0013] 101 kg basisches Aluminiumcarbonat (19,15 % Al_2O_3) wurden in 8,3 kg Wasser und 14,5 kg Ameisensäure 85 %ig aufgeschlämmt und mit 65,1 kg Aluminiumsulfat (17,5 % Al_2O_3) versetzt. Unter Rühren wurde bei einer Temperatur von 33 bis 62 °C nach 4 Stunden eine fast klare Lösung erhalten.

Beispiel 6

[0014] In 500 g der Lösung aus Beispiel 5 wurden 67,7 g Magnesiumsulfat (27,5 MgO) gelöst.

Beispiel 7

[0016] 105,5 g Aluminiumtrifluorid (11,7 % Al, 81,3 % Amleersäure) wurden mit 358,3 g basischem Aluminiumcarbonatsulfat (18,4 % Al_2O_3) und 375 g Aluminumsulfat (17,5 % Al_2O_3) vermischt. Unter Röhren wurde bei einer Temperatur von 75 °C nach 90 min eine leicht trübe Lösung erhalten.

Vergleichsbeispiel 1:

[0016] Dispersion eines basischen Aluminiumcarbonatsulfates mit 18,5 % Al_2O_3

Vergleichsbeispiel 2:

[0017] Dispersion eines basischen Aluminumsulfates mit 18 % Al_2O_3

Tabelle 1

Wirkung der erfindungsgemäßen Verbindungen auf die Abbindezeiten				
Beschleuniger aus	Konz. bezgl. Portlandzement	Zement	Abbindeanfang (sec)	Abbindeende (sec)
Beispiel 1	10 %	A	185	300
Beispiel 2	10 %	A	240	450
Beispiel 3	10 %	A	240	380
Beispiel 4	7,3 %	B	75	180
Beispiel 5	6 %	C	135	240
Beispiel 6	7,5 %	B	80	200
Beispiel 7	8,5 %	B	90	240
Vergleichsbeispiel 1	5 %	A	>500	n.b.
Vergleichsbeispiel 1	10 %	A	>500	n.b.
Vergleichsbeispiel 2	5 %	A	>500	n.b.
Vergleichsbeispiel 2	10 %	A	>500	n.b.
Vergleichsbeispiel 1	10 %	B	>500	n.b.
Vergleichsbeispiel 1	10 %	C	>500	n.b.

[0018] A, B und C sind Portlandzemente verschiedener Hersteller.

[0018] Die Abbindezeiten wurden in Anlehnung an die Vicat-Methode ermittelt. Eingesetzt wurden jeweils 280 g Portlandzement und 2,9 g Verflüssiger (1%). Der W/Z Wert betrug 0,41. Der Zementleim wurde 90 min gerührt und danach beschleunigt.

Versuche im Naßspritzverfahren mit den erfindungsgemäßen Abbindebeschleunigern

[0020] Maschine: Schwing Betonpumpe PB 750 RE mit Beschleuniger-Dosiereinrichtung Top-Shot Düse

Schlauchdurchmesser	65 mm
Spritzschlauchdurchmesser	50 mm
Spritzschlauchlänge	5 m
Materieldurchsatz in kg/min	162
Rückprall in %	3,5
Bleblinie	B8
Zementgehalt des PZ- C in kg/m³	425

(fortgesetzt)

W/Z-Wert	0,485
Verflüßiger in %	1,3
Verzögerer in %	0,1
Beschleuniger	aus Beispiel 5, 6,6 %
Frühfestigkeit	Kalnd-Meyco Verfahren
Festbetonprüfung	Bohrkern Ø 10 cm
Ausbreitmaß	ca. 50 cm

Tabelle 2:

Druckfestigkeiten in N/mm²		
Zeit	Beschleuniger aus Beispiel 5, 6,6 %	ohne Beschleuniger
1 h	1,4	-
2 h	2,0	-
4 h	3,7	-
6 h	6,9	-
8 h	9,5	-
24 h	14,1	-
2 d	29	-
7 d	38	-
28 d	51	55

[0021] Alle Daten basieren auf 2 Parallelversuchen

Tabelle 3:

Wirkung der erfindungsgemäßen Verbindungen auf die Frühfestigkeitsentwicklung				
Frühfestigkeiten in N/mm² mit Beschleunigern aus :				
Zeit(h)	Bep. 4 (5,9 %)	Bep. 6 (6,7%)	Bep. 4 (gefrost. 5,9%)	Bep. 6 (gefrost. 6)
2	1,41	1,56	1,5	1,6
6	4,5	5,4	4,9	6,2
8	5,8	7,2	6,1	8,2
24	17,9	21,8	19,0	22,5

[0022] Die Festigkeiten wurden in Anlehnung an DIN 1164, Teil 7 untersucht. Dabei wurden folgende Modifikationen vorgenommen:

Zuschlag: 0-8 mm
W/Z Wert: 0,55
Verflüßiger: 1,5 %
Beschleunigerzugabe: 60 min nach Herstellung des Betons
Portlandzement: 400 kg/m³
(Sorte B)

Patentansprüche

1. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel, erhältlich durch ein Verfahren, das dadurch gekennzeichnet ist, daß folgende Komponenten

Komponente a: basische Aluminiumsalze und/oder Aluminiumhydroxyd
 Komponente b: Aluminiumsulfat und/oder Schwefelsäure
 Komponente c: organische Carbonsäuren oder Mischungen zumindest zwei der organischen Carbonsäuren
 Komponente d: Aluminiumsalze der organischen Carbonsäuren
 Komponente e: organische und/oder anorganische Sulfate und/oder Hydrogensulfate und/oder Carbonate und/oder Hydrogencarbonate und/oder Erdalkalioxyde und/oder Erdalkalhydroxyde

bei Temperaturen bis 150 °C in Wasser zur Reaktion gebracht werden, so daß dabei eine Lösung erhalten wird, wobei

1. alle Komponenten oder eine Auswahl der Komponenten miteinander reagieren, so daß die Molverhältnisse des Aluminiums zu Sulfat im Endprodukt 0,83 bis 13,3 und die Molverhältnisse des Aluminiums zur organischen Carbonsäure 0,67 bis 33,3 betragen oder
2. alle Komponenten außer Komponente e oder eine Auswahl der Komponenten außer Komponente e miteinander reagieren, so daß die Molverhältnisse des Aluminiums zu Sulfat im Endprodukt 0,83 bis 13,9 und die Molverhältnisse des Aluminiums zur organischen Carbonsäure im Endprodukt 0,67 bis 33,9 betragen oder
3. die Komponente e nachträglich im Reaktionsprodukt nach Punkt 2, aufgelöst wird.

2. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel nach Anspruch 1, dadurch gekennzeichnet, daß als basische Aluminiumsalze die basischen Sulfate, Carbonate, Carbonatsulfate und Nitrate und Mischungen von mindestens zwei dieser Komponenten eingesetzt werden.
3. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel nach den Ansprüchen 1 und 2, dadurch gekennzeichnet, daß als organische Carbonsäuren Monocarbonsäuren Hydroxycarbonsäuren und Dicarbonsäuren und deren Mischungen eingesetzt werden.
4. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel nach den Ansprüchen 1 bis 3, dadurch gekennzeichnet, daß als Sulfate bzw. Hydrogensulfate die Erdalkalisalze und/oder Triethanolaminsalze und/oder Diethanolaminsalze der Schwefelsäure verwendet werden.
5. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel nach den Ansprüchen 1 bis 4, dadurch gekennzeichnet, daß als Carbonate die Erdalkalicarbonate und als Hydrogencarbonate die Erdalkalhydrogencarbonate verwendet werden.
6. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel nach den Ansprüchen 1 bis 5, dadurch gekennzeichnet, daß als organische Carbonsäuren Ameisensäure, Essigsäure, Glycolsäure, Milchsäure und Mischungen von mind. zwei dieser Komponenten eingesetzt werden.
7. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel nach den Ansprüchen 1 bis 6, dadurch gekennzeichnet, daß als Sulfate bzw. Hydrogensulfate die Alkalisalze der Schwefelsäure verwendet werden.
8. Erstarrungs- und Erhärtungsbeschleuniger für hydraulische Bindemittel nach den Ansprüchen 1 bis 7, dadurch gekennzeichnet, daß sie in Kombination mit anderen Verbindungen, wie z.B. mit Abbindeverzögerern, Verflüssigern oder Rückprallvermindernern eingesetzt werden.
9. Zement, Mörtel und Beton enthaltend die Erstarrungs- und Erhärtungsbeschleuniger gemäß den Ansprüchen 1 bis 8

Claims

1. Solidifying and hardening accelerator for hydraulic binders, obtainable by a process which is characterised in that the following components:

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component a: basic aluminium salts and/or aluminium hydroxide

component b: aluminium sulphate and/or sulphuric acid

component c: organic carboxylic acids or mixtures of at least two of the organic carboxylic acids

component d: aluminium salts of the organic carboxylic acids

component e: organic and/or inorganic sulphates and/or hydrogen sulphates and/or carbonates and/or hydrogen carbonates and/or alkaline earth metal oxides and/or alkaline earth metal hydroxides

are reacted in water at temperatures of up to 160°C, so as to obtain a solution, whilst

1. all the components or a selection of the components react with one another so that the molar ratios of the aluminium to sulphate in the end product are from 0.83 to 13.3 and the molar ratios of the aluminium to the organic carboxylic acid are 0.67 to 33.3 or

2. all the components apart from component e or a selection of the components apart from component e react with one another, so that the molar ratios of the aluminium to sulphate in the end product are from 0.83 to 13.3 and the molar ratios of the aluminium to the organic carboxylic acid in the end product are from 0.67 to 33.3 or

3. component e is subsequently dissolved in the reaction product according to point 2.

2. Solidifying and hardening accelerator for hydraulic binders according to claim 1, characterised in that the basic sulphates, carbonates, carbonate sulphates and nitrates and mixtures of at least two of these components are used as basic aluminium salts.

3. Solidifying and hardening accelerator for hydraulic binders according to claims 1 and 2, characterised in that mono-carboxylic acids, hydroxycarboxylic acids and dicarboxylic acids and mixtures thereof are used as organic carboxylic acids.

4. Solidifying and hardening accelerator for hydraulic binders according to claims 1 to 3, characterised in that the alkaline earth metal salts and/or triethanolamine salts and/or diethanolamine salts of sulphuric acid are used as the sulphates or hydrogen sulphates.

5. Solidifying and hardening accelerator for hydraulic binders according to claims 1 to 4, characterised in that the alkaline earth metal carbonates are used as the carbonates and the alkaline earth metal hydrogen carbonates are used as the hydrogen carbonates.

6. Solidifying and hardening accelerator for hydraulic binders according to claims 1 to 5, characterised in that formic acid, acetic acid, glycolic acid, lactic acid and mixtures of at least two of these components are used as the organic carboxylic acids.

7. Solidifying and hardening accelerator for hydraulic binders according to claims 1 to 6, characterised in that the alkali metal salts of sulphuric acid are used as the sulphates or hydrogen sulphates.

8. Solidifying and hardening accelerator for hydraulic binders according to claims 1 to 7, characterised in that they are used in conjunction with other compounds, such as, for example, with setting retarders, liquefiers or resilience reducers.

9. Concrete, mortar and cement containing the solidifying and hardening accelerator according to the claims 1 to 8.

Revendications

1. Accélérateur de solidification et de prise pour liants hydrauliques, pouvant être obtenu par un procédé qui est caractérisé en ce que l'on fait réagir les composants suivants :

composant a : sel basique d'aluminium et/ou hydroxyde d'aluminium ;

composant b : sulfate d'aluminium et/ou acide sulfurique ;

composant c : acide carboxylique organique ou mélange d'au moins deux acides carboxyliques organiques ;

composant d : sel d'aluminium des acides carboxyliques organiques ;

composant e : sulfite et/ou hydrogénosulfate et/ou carbonate et/ou hydrogénocarbonate organiques et/ou inorganiques, et/ou oxyde alcalino-terreux et/ou hydroxyde alcalino-terreux.

dans l'eau à une température de jusqu'à 150°C, de sorte que l'on obtienne une solution, où

1- tous les composants ou un choix des composants réagissent les uns avec les autres, de sorte que le rapport molaire de l'aluminium au sulfate se situe dans le produit final, dans l'intervalle allant de 0,83 à 13,3 et le rapport molaire de l'aluminium à l'acide carboxylique organique se situe dans l'intervalle allant de 0,67 à 33,3, ou

2- tous les composants sauf le composant e ou un choix des composants sauf le composant e réagissent les uns avec les autres, de sorte que le rapport molaire de l'aluminium au sulfate se situe dans le produit final, dans l'intervalle allant de 0,83 à 13,3 et le rapport molaire de l'aluminium à l'acide carboxylique organique dans le produit final, se situe dans l'intervalle allant de 0,67 à 33,3, ou

3- le composant e est dissous ultérieurement dans le produit de réaction du point 2.

2. Accélérateur de solidification et de prise pour liants hydrauliques suivant la revendication 1, caractérisé en ce que l'on met en oeuvre comme sel basique d'aluminium, un sulfate, carbonate, carbonatesulfate, nitrate basiques ou mélanges d'au moins deux de ces composants.

3. Accélérateur de solidification et de prise pour liants hydrauliques suivant les revendications 1 et 2, caractérisé en ce que l'on met en oeuvre comme acide carboxylique organique, un monoacide carboxylique, un acide hydroxycarboxylique, un diacide carboxylique ou leurs mélanges.

4. Accélérateur de solidification et de prise pour liants hydrauliques suivant les revendications 1 à 3, caractérisé en ce que l'on utilise comme sulfate ou hydrogènesulfate, un sel alcalino-terreux et/ou sel de triéthanolamine et/ou sel de diéthanolamine de l'acide sulfurique.

5. Accélérateur de solidification et de prise pour liants hydrauliques suivant les revendications 1 à 4, caractérisé en ce que l'on utilise comme carbonate, un carbonate alcalino-terreux et comme hydrogénocarbonate, un hydrogénocarbonate alcalino-terreux.

6. Accélérateur de solidification et de prise pour liants hydrauliques suivant les revendications 1 à 5, caractérisé en ce que l'on met en oeuvre comme acide carboxylique organique, l'acide formique, l'acide acétique, l'acide glycolique, l'acide lactique et les mélanges d'au moins deux de ces composants.

7. Accélérateur de solidification et de prise pour liants hydrauliques suivant les revendications 1 à 6, caractérisé en ce que l'on utilise comme sulfate et respectivement, hydrogènesulfate, un sel alcalin de l'acide sulfurique.

8. Accélérateur de solidification et de prise pour liants hydrauliques suivant les revendications 1 à 7, caractérisé en ce qu'il est mis en oeuvre avec d'autres composés, comme par exemple un retardateur de prise, un fluidifiant ou un agent de diminution du rebondissement.

9. Ciment, mortier et béton contenant l'accélérateur de solidification et de prise suivant les revendications 1 à 8.

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(54) **CEMENT ACCELERATING ADMIXTURE**
ABBINDEBESCHLEUNIGER FÜR CEMENT
ADDITIF ACCELERATEUR POUR CIMENT

(84) Designated Contracting States: AT CH DE ES FR GB IT LI SE (30) Priority: 10.08.1994 GB 9418114 (43) Date of publication of application: 28.05.1997 Bulletin 1997/22 (73) Proprietor: MBT HOLDING AG 8048 Zürich (CH) (72) Inventor: LEIKAUF, Bernhard CH-5224 Linn (CH)	(56) References cited: <table><tr><td>EP-A- 0 692 783</td><td>DE-A- 2 122 710</td></tr><tr><td>DE-A- 3 738 258</td><td>FR-A- 2 031 680</td></tr></table> • DATABASE WPI Section Ch, Week 7802 Derwent Publications Ltd., London, GB; Class E33, AN 78-03338A & JP,A,52 141 837 (ASADA KAGAKU KOGYO), 28 November 1977 • PATENT ABSTRACTS OF JAPAN vol. 015 no. 167 (C-0827), 25 April 1991 & JP,A,03 037145 (OSAKA CEMENT CO LTD) 18 February 1991, • CHEMICAL ABSTRACTS, vol. 97, no. 20, 18 November 1982 Columbus, Ohio, US; abstract no. 157913, KUZNETSOVA & AL. 'Increasing the strength of high alumina cements' & SZLIKATIP, SZLIKATTUD. KONF. PROM., vol. 3, 1991 pages 151-158,	EP-A- 0 692 783	DE-A- 2 122 710	DE-A- 3 738 258	FR-A- 2 031 680
EP-A- 0 692 783	DE-A- 2 122 710				
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Description

This invention relates to cementitious spraying compositions and to admixtures for use therein.

5 Cementitious compositions for application to a substrate by spraying, for example, "shotcrete", must be capable of being sprayed in the first place (that is, they must retain sufficient fluidity), and on contacting the surface, they must set quickly (generally within a few minutes) to give a stiff layer to which further layers may quickly be applied. The art-recognized way of achieving this has been the addition at the point of spraying (for example, by injecting into a spray nozzle) of an accelerator in the form of an aqueous solution. The accelerators used are generally strong alkalis such as sodium aluminate, sodium or potassium hydroxide or carbonate and triethanolamine (see, for example, "Concrete

10 Admixtures Handbook", ed. Ramachandran (Noyes, 1984)).

The nature of such substances makes for unpleasant working conditions on spraying sites, and there has long been a need for an effective spraying accelerator which has less of the caustic character of the known accelerators. In a recent development, accelerators comprising amorphous aluminium hydroxide have been proposed. These have the advantage of low alkalinity and high performance. Typical examples of accelerators have been blends of amorphous

15 aluminium hydroxide with gypsum or various water-soluble salts.

Accelerators applied at the nozzle are in liquid form. This means that, in the case of aluminium hydroxide, the solid accelerator must be dispersed in water. This can be done on site, but it is much more convenient if such an accelerator can be supplied in liquid form. This has hitherto not been possible with aluminium hydroxide, dispersions of which are not storage-stable for more than a few days.

20 It has now been found that a particular combination of aluminium hydroxide with another material not only has excellent storage stability but also is particularly effective as an accelerator for spraying cementitious compositions. There is therefore provided, according to the present invention, an accelerating admixture for use in the spraying of cementitious composition, comprising (a) amorphous aluminium hydroxide and/or aluminium hydroxysulphate, and (b) at least one amine, the constituents (a) and (b) being components of a single admixture.

25 There is additionally provided a method of preparing a storage-stable, amorphous aluminium hydroxide and/or aluminium hydroxysulphate-based accelerating admixture by the dispersion of amorphous aluminium hydroxide and/or aluminium hydroxysulphate in water, there being additionally added at least one amine.

In the particular circumstances of this invention, aluminium hydroxysulphate is often a better accelerator than aluminium hydroxide and is therefore preferred. It is possible to use a mixture of aluminium hydroxysulphate with aluminium hydroxide and/or aluminium sulphate, but it is preferable to use the hydroxysulphate alone. A typical commercially-available aluminium hydroxysulphate is "Gecedra" (trade mark) L (of Guillin Chemie GmbH, Ludwigshafen/Rhein, Germany).

30 The amines for use in this invention should be liquid or soluble in water. A highly preferred class of amines is that of the alkanolamines. The preferred alkanolamines are dialkanolamines and trialkanolamines, more preferably diethanolamine and triethanolamine. Most preferred is a mixture of diethanolamine and triethanolamine.

In an admixture according to the invention, the aluminium hydroxide and/or hydroxysulphate is combined with the alkanolamine in the weight ratio of from 1:10 - 1000:1, preferably from 1:10 - 100:1, more preferably from 1:1 - 10:1. When the preferred mixture of diethanolamine and triethanolamine is used, the ratio of diethanolamine to triethanolamine is from 1:1 to 0:1.

35 The constituents of the admixture are added to a spray nozzle as a pre-mixed blend. The invention therefore also provides an accelerating admixture which is a mixture of the aforementioned amorphous aluminium hydroxide and/or aluminium hydroxysulphate and amine constituent. The weight ratio of the constituent on cement is from 0.5-10% for the aluminium hydroxide/hydroxysulphate and from 0.001 to 5%, more preferably from 0.001 - 2% or 0.01 - 5% for the amine.

40 In an especially preferred embodiment of the invention, the accelerating admixture of the invention may be combined with certain other materials to provide particularly outstanding results. The invention therefore also provides a spraying admixture which comprises a combination of an accelerating admixture as hereinabove defined and an aqueous dispersion of at least one polymer which comprises pendant carboxylic moieties.

45 The polymers useful in this aspect of the invention are any polymers which bear suitable pendant carboxylic moieties. The carboxylic moiety may be a carboxyl group, and any polymer having such groups and complying with the other parameters hereinunder described will work in this invention. Examples include poly(acrylic) and poly(methacrylic) acids and mixtures thereof and copolymers of (meth)acrylic acid with other comonomers. However, preferred polymers are of the "comb" type, that is, polymers comprising a polymer backbone (whose chemical nature is irrelevant to the working of the invention) with carboxyl group-containing moieties pendant therefrom. The moieties may be up to 100 units long and may comprise monomer residues of, for example (meth)acrylic acid, maleic acid or fumaric acid. It is preferred that the moieties be completely made up of (meth)acrylic acid residues.

50 A preferred backbone is a random addition polymer, one of the monomers of which comprised, prior to polymerization, more than one, and preferably two, polymerizable double bonds. A preferred monomer with more than one

double bond is butadiene and a preferred copolymer is a styrene-butadiene copolymer. To such a copolymer (which may have pendant and/or in-chain polymerizable double bonds) carboxyl group-containing monomers such as acrylic acid, methacrylic acid, maleic acid or fumaric acid may be graft copolymerized. Examples of preferred copolymers are styrene-butadiene copolymerized with acrylic acid and styrene-butadiene/maleic (or fumaric) acid terpolymer.

The polymers of this invention have molecular weights (weight average) in excess of 20,000 and are solids at room temperature. They also have a limited solubility in water, being at best dispersible (never completely soluble), but they are highly soluble in alkaline media (such as a fluid cementitious mix). In the case of poly(meth)acrylic acid and polymers which are inherently soluble in water, it is possible to prepare such polymers in such a form that the necessary solubility is achieved, for example, particulate form. They are added to the cementitious mix as an aqueous dispersion of less than 5% solids by weight.

Typical examples of suitable commercial materials are those available under the trade mark "Synthomer" (ex Synthomer Chemie GmbH, Frankfurt/Main, Germany). An especially suitable example is "Synthomer" 8523 (a methacrylic acid-styrene-butadiene copolymer). Another suitable commercial product is "Polyacryl" AD (ex Polygon Chemie AG, Olten, Switzerland).

The aqueous dispersion is added to the cementitious composition at the nozzle, either separately from or in a mixture with the accelerating admixture hereinabove described. The proportion of polymer present is from 0.01 to 3% by weight on cement.

When the spraying admixture comprises an aqueous polymer dispersion as hereinabove described, the admixture must be acid, preferably with a pH of 8 maximum. This may be achieved by the addition of an acid, which may be chosen from any suitable strong organic or inorganic acid, which is added in sufficient quantity to achieve the desired pH. In addition, the acid must not react adversely with any of the components of the cementitious composition or the admixture to an unacceptable degree. Reactivity will vary, depending on the individual acid and the components present, but the selection of a suitable acid is not a problem for the skilled person. It is preferred to use a strong mineral acid, and nitric acid has been found to work particularly well in most circumstances.

It has been found that the use of an aqueous polymer dispersion as hereinabove defined in conjunction with an accelerating admixture as hereinabove described enhances the performance of a sprayed cementitious composition considerably. In particular, it appears to enhance adhesion of the sprayed composition to the substrate in the important few minutes after spraying when the hardening of the composition is not sufficiently advanced to ensure good adhesion.

A preferred spraying admixture has the following composition (dry contents, by weight, the remainder of the formulation to 100% being water):

aluminium hydroxide/hydroxysulphate	20% - 80%	✓
alkanolamine	0.01% - 25%	✓
polymer dispersion	0% - 20%	
acid	1% - 20%	✓

A particularly preferred composition has the composition (dry contents, by weight, the remainder of the formulation to 100% being water)

aluminium hydroxysulphate	40% - 80%
triethanolamine	0.01% - 20%
diethanolamine	0% - 5%
acrylic copolymer dispersion	10% - 20%
nitric acid	5% - 20%

The compositions and processes of this invention are useful in the spraying of cementitious composition by both the "wet" and "dry" methods, but they work better in the "wet" method where water is added at the mixing stage prior to pumping. The invention therefore provides a sprayable cementitious composition which comprises an admixture as hereinabove defined.

The sprayable compositions according to this invention may also comprise any of the wide range of other admixtures known to be useful in sprayable cementitious compositions, used in art-recognised quantities. One particularly useful category of admixture is that of the plasticisers and superplasticisers; these can assist in the achievement of a desirable water/cement (W/C) ratio. A further class of useful admixtures are set retarders. Any of the known types may be used, a particularly useful class of materials being phosphonic acid-based materials, in particular those described in United States Patent 4,954,917.

A particular feature of the invention is the excellent storage stability of the admixtures according to the invention.

if aluminium hydroxide and/or aluminium hydroxysulphate is dispersed in water, the viscosity rises rapidly to a value which renders the mixture unusable very quickly (typically LVT Brookfield viscosity 100,000+ mPas (Spindle No.4 at 1.5 rpm) a few days after mixing and completely solid after one week). In contrast, an admixture according to the present invention stored at 20°C remains usable for 6 months. Thus, it is possible to prepare admixtures well in advance of use and have them immediately ready, thus reducing the need to mix on site.

Spraysable cementitious compositions which utilize this invention form thick layers which "set up" quickly and can be resprayed without any problems. Rebound characteristics are particularly good, as are both strength development and long term strength. The invention therefore provides the use of a mixture of aluminium hydroxide and/or hydroxysulphate and at least one amine as an accelerating admixture for cementitious compositions which are to be sprayed.

The invention further provides a method for the spraying of a cementitious composition on to a substrate from a spray nozzle, wherein there is added to the composition at the nozzle an accelerating admixture as hereinabove defined.

The invention is further described with reference to the following examples in which all parts are expressed by weight.

(a) Preparation of spraying admixture The following materials are blended under low shear to form a homogeneous mixture:

water	55 parts
aluminium hydroxysulphate ¹	17.8
triethanolamine	7.7
diethanolamine	1.55
65% nitric acid	7.7
aqueous polymer dispersion ²	6.15

1. "Gossard" L. or Gossard Chemie
2. "Syntheser" 9823 or T16b Chemie

(b) Testing of spraying admixture

(i) A spraying concrete mixture is prepared with a W/C ratio of about 0.45. The mixture is sprayed on to a substrate through a nozzle with a dosing at the nozzle with the spraying admixture of 4.8% by weight on cement. It is found that the sprayed concrete goes matt immediately (signifying immediate setting) and that a layer of thickness in excess of 25cm. can quickly be built up with very little rebound. A measurable strength develops after only 6 minutes, and after 16 hours the strength (measured at a number of different points) is between 7 and 18.8 N/mm².

(ii) The procedure of (i) above is repeated with a dosing of 3.8%. In this case, the thickness readily achievable is about 20cm. and early strength development becomes measurable after about 20 min. After 16 hours, strength is measured and found to be between 14.7 and 19.6 N/mm².

- Claims
1. An accelerating admixture for use in the spraying of cementitious compositions, comprising (a) amorphous aluminium hydroxide and/or aluminium hydroxysulphate, and (b) at least one amine, the constituents (a) and (b) being components of a single admixture.
 2. An accelerating admixture according to claim 1, consisting of a mixture of constituents (a) and (b).
 3. An accelerating admixture according to claim 1 or claim 2, wherein aluminium hydroxysulphate is used and aluminium hydroxide is excluded.
 4. An accelerating admixture according to any one of claims 1 - 3, wherein the amine is an alkanolamine, preferably a dialkanolamine or trialkanolamine, more preferably diethanolamine or triethanolamine, most preferably a mixture of diethanolamine and triethanolamine.
 5. An accelerating admixture according to any one of claims 1 and 3-4, wherein the admixture additionally comprises an aqueous dispersion of at least one polymer which comprises pendant carboxylic moieties, preferably a "comb"-type polymer.

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6. A spraying admixture with the following composition (dry contents, by weight, water to 100%):

aluminium hydroxide/hydroxysulphate	20% - 80%
alkanolamine	0.01% - 25%
polymer dispersion	0% - 10%
acid	1% - 20%

7. The use of a mixture of aluminium hydroxide and/or hydroxysulphate and at least one amine as an accelerating admixture for cementitious compositions which are to be sprayed.

8. A method of preparing a storage-stable, amorphous aluminium hydroxide and/or aluminium hydroxysulphate-based accelerating admixture by the dispersion of amorphous aluminium hydroxide and/or aluminium hydroxysulphate in water, there being additionally added at least one amine.

9. A method for the spraying of a cementitious composition on to a substrate from a spray nozzle, wherein there is added to the composition at the nozzle an accelerating admixture according to any one of claims 1-6.

10. A sprayable cementitious composition which comprises an admixture according to any one of claims 1-6

Patentansprüche

1. Beschleunigerbeimischung zur Verwendung beim Spritzen von Zementzusammensetzungen, umfassend (a) amorphes Aluminiumhydroxid und/oder Aluminiumhydroxysulfat und (b) wenigstens ein Amin, wobei die Bestandteile (a) und (b) Bestandteile einer einzelnen Beimischung sind.

2. Beschleunigerbeimischung nach Anspruch 1, bestehend aus einer Mischung der Bestandteile (a) und (b).

3. Beschleunigerbeimischung nach Anspruch 1 oder 2, worin Aluminiumhydroxysulfat verwendet wird und Aluminiumhydroxid ausgeschlossen ist.

4. Beschleunigerbeimischung nach einem der Ansprüche 1 bis 3, worin das Amin ein Alkanolamin, vorzugsweise ein Diäkanolamin oder Triäkanolamin, bevorzugter Diethanolamin oder Triethanolamin, und besonders bevorzugt eine Mischung aus Diethanolamin und Triethanolamin ist.

5. Beschleunigerbeimischung nach einem der Ansprüche 1 und 3 bis 4, worin die Beimischung zusätzlich eine wässrige Dispersion aus wenigstens einem Polymer enthält, das pendantes Carbonsäurereste aufweist und das vorzugsweise ein kammartiges Polymer ist.

6. Spritzbeimischung mit der folgenden Zusammensetzung (auf Trockengewicht bezogen und mit Wasser auf 100% ergänzt):

Aluminiumhydroxid/Aluminiumhydroxysulfat	20% bis 80%
Alkanolamin	0,01% bis 25%
Polymerdispersion	0% bis 10%
Säure	1% bis 20%

7. Verwendung einer Mischung aus Aluminiumhydroxid und/oder Aluminiumhydroxysulfat und aus wenigstens einem Amin als Beschleunigerbeimischung für Zementzusammensetzungen, die gespritzt werden sollen.

8. Verfahren zur Herstellung einer lagerstabilen Beschleunigerbeimischung auf Basis von amorphem Aluminiumhydroxid und/oder Aluminiumhydroxysulfat durch Dispergierung von amorphem Aluminiumhydroxid und/oder Aluminiumhydroxysulfat in Wasser unter weiterem Zusatz von wenigstens einem Amin.

9. Verfahren zum Spritzen einer Zementzusammensetzung auf einen Träger aus einer Spritzdüse, wobei der Zusammensetzung an der Düse eine Beschleunigerbeimischung nach einem der Ansprüche 1 bis 6 zugesetzt wird.

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10. Spritzementzusammensetzung, die eine Belmischung nach einem der Ansprüche 1 bis 6 enthält.

Revendications

1. Mélange accélérateur pour l'utilisation dans la pulvérisation de compositions cimentières, comprenant (a) un hydroxyde d'aluminium et/ou hydroxysulfate d'aluminium amorphes et (b) au moins une amine, les constituants (a) et (b) étant des constituants d'un seul mélange.
2. Mélange accélérateur selon la revendication 1, constitué par un mélange des constituants (a) et (b).
3. Mélange accélérateur selon la revendication 1 ou la revendication 2, dans lequel l'hydroxysulfate d'aluminium est utilisé et l'hydroxyde d'aluminium est exclu.
4. Mélange accélérateur selon l'une quelconque des revendications 1-3, dans lequel l'amine est une alcanolamine, de préférence une dialcanolamine ou une trialcanolamine, de préférence encore la diéthanolamine ou la triéthanolamine, de toute préférence un mélange de diéthanolamine et de triéthanolamine.
5. Mélange accélérateur selon l'une quelconque des revendications 1 et 3-4, dans lequel le mélange comprend en plus une dispersion aqueuse d'au moins un polymère qui comprend des fractions carboxyliques pendantes, de préférence un polymère de type "peigne".
6. Mélange à pulvériser ayant la composition suivante (teneurs en matières sèches, en poids, eau à 100 %):

hydroxyde/hydroxysulfate d'aluminium	20 % - 60 %
alcanolamine	0,01 % - 25 %
dispersion de polymère	0 % - 10 %
acide	1 % - 20 %

7. Utilisation d'un mélange d'hydroxyde et/ou hydroxysulfate d'aluminium et d'au moins une amine en tant que mélange accélérateur pour des compositions cimentières qui doivent être pulvérisées.
8. Procédé de préparation d'un mélange accélérateur à base d'hydroxyde d'aluminium et/ou hydroxysulfate d'aluminium amorphes, stable au stockage, par la dispersion d'hydroxyde d'aluminium et/ou hydroxysulfate d'aluminium amorphes dans de l'eau, en ajoutant en plus au moins une amine.
9. Procédé pour pulvériser une composition cimentière sur un substrat à partir d'une buse de pulvérisation dans lequel on ajoute à la composition, à la buse, un mélange accélérateur selon l'une quelconque des revendications 1-6.
10. Composition cimentière pulvérisable, qui comprend un mélange selon l'une quelconque des revendications 1-6.

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NOUVEAU TRAITE DE CHIMIE MINÉRALE

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BORE — ALUMINIUM — GALLIUM — INDIUM — THALLIUM

PAR MM.

P. PASCAL, A. CHRÉTIEN, Y. TRAMBOUZE, J.-C. MUTTER,
W. FREUNDLICH

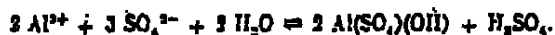
MASSON ET C^e, ÉDITEURS

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1961

SULFATES D'ALUMINIUM BASIQUES

L'hydrolyse classique d'une solution de sulfate d'aluminium convenablement diluée devrait conduire au sel basique selon la réaction :



En réalité, la composition du précipité obtenu n'est pas parfaitement définie.

La vitesse de l'hydrolyse croît avec la dilution de la solution et avec la température (Denham) ⁽¹⁷⁾, (Lay) ⁽¹⁸⁾, (Kahlenberg, Davis et Fowler) ⁽¹⁹⁾, (Bruner) ⁽²⁰⁾, (Carrara et Vespignani) ⁽²¹⁾.

A haute température : 234,5 °C et sous 30 atm se produit une hydrolyse réversible qui conduirait au sulfate basique $3 \text{Al}_2\text{O}_3, 4 \text{SO}_3, 7 \text{H}_2\text{O}$ (Bratsanaïder et Kaweckij) ⁽²²⁾.

L'action de l'acide sulfurique sur l'aluminium amalgamé conduit aux phases cristallisées suivantes (Bassett et Goodwin) ⁽²³⁾ : $\text{Al}_2\text{O}_3, 3 \text{SO}_3, 16 \text{H}_2\text{O}$; $\text{Al}_2\text{O}_3, 2 \text{SO}_3, 11 \text{H}_2\text{O}$; $5 \text{Al}_2\text{O}_3, 6 \text{SO}_3, 46 \text{H}_2\text{O}$; $\text{Al}_2\text{O}_3, \text{SO}_3, 9 \text{H}_2\text{O}$ (aluminite) ; $\text{Al}_2\text{O}_3, \text{SO}_3, 6,78 \text{H}_2\text{O}$; $2 \text{Al}_2\text{O}_3, \text{SO}_3, 30 \text{H}_2\text{O}$; $2 \text{Al}_2\text{O}_3, \text{SO}_3, 10 \text{H}_2\text{O}$; $5 \text{Al}_2\text{O}_3, 3 \text{SO}_3, 33 \text{H}_2\text{O}$; $7 \text{Al}_2\text{O}_3, 3 \text{SO}_3, 33 \text{H}_2\text{O}$; $11 \text{Al}_2\text{O}_3, 6 \text{SO}_3, 66 \text{H}_2\text{O}$; $13 \text{Al}_2\text{O}_3, 6 \text{SO}_3, 83 \text{H}_2\text{O}$.

Lorsque l'on fait bouillir une solution d'acide chlorhydrique normale ou dixième normale en présence d'aluminium, on obtient un chlorure dans lequel le rapport $\text{Al}/\text{Cl} = 1/0,5$. Si à cette solution on ajoute du sulfate de sodium on obtient le sulfate basique $(\text{Al}_2(\text{OH})_2)_2\text{SO}_4$ (Deuk et Bauer) ⁽²⁴⁾.

Le sel de Williamson $5 \text{Al}_2\text{O}_3, 3 \text{SO}_3, 15 \text{H}_2\text{O}$ obtenu à partir de soude et d'alun, peut s'obtenir également par action du carbonate acide de sodium sur le sulfate d'aluminium (Le Peintre) ⁽²⁵⁾. L'électrolyse de ce sel conduit à admettre l'existence d'un anion complexe dont la formule n'a pu être établie d'une façon certaine ⁽²⁶⁾.

L'hydrogel d'alumine se dissout dans une solution aqueuse de sulfate d'aluminium, d'autant plus rapidement qu'il est de préparation plus récente. L'étude de cette solubilité en fonction de la concentration, pour diverses températures, a révélé les composés : $\text{Al}_2\text{O}_3, \text{SO}_3, 9 \text{H}_2\text{O}$; $\text{Al}_2\text{O}_3, 2 \text{SO}_3, 12 \text{H}_2\text{O}$ et $\text{Al}_2(\text{SO}_4)_3, 16 \text{H}_2\text{O}$ (Kreimann et Mullinger) ⁽²⁷⁾.

D'autres sulfates basiques signalés — (Schmatolla) ⁽²⁸⁾, (Berzélius) ⁽²⁹⁾, (Bley) ⁽³⁰⁾ — ne seraient que des stades intermédiaires de l'hydrolyse, leur composition dépendant des circonstances de préparation.

L'hydrate $\text{Al}_2\text{SO}_4(\text{OH})_2, 7 \text{H}_2\text{O}$, de densité 1,705 et de dureté comprise entre 1 et 2, est représenté par l'aluminite (Karsten) ⁽³¹⁾, la hallite (Delametherie) ⁽³²⁾, la ruine lonerda (Werner) ⁽³³⁾, l'argile native (Kirman) ⁽³⁴⁾, la webstérite (Brooke) ⁽³⁵⁾, (Beudant) ⁽³⁶⁾.

La décomposition ménagée de l'alun d'ammonium par la chaleur fournit d'abord du sulfate d'aluminium anhydre ; puis il y a volatilisation de l'acide sulfurique. Un réglage convenable du chauffage permet de récupérer finalement un résidu entièrement soluble dans l'eau, consistant principalement en sulfate basique $\text{Al}_2\text{O}_3, 2 \text{SO}_3, 10 \text{H}_2\text{O}$ ou $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2, 11 \text{H}_2\text{O}$ (Margue-

~~SECRET~~ D4

United States Patent [19]
Carpenter et al.

[11] **Patent Number:** **4,976,316**
[45] **Date of Patent:** **Dec. 11, 1990**

[54] **METHOD OF ACCELERATING SET OF CEMENT BY WASHOVER FLUID CONTAINING ALKANOLAMINE**
[75] **Inventors:** Robert B. Carpenter, Hurst; William N. Wilson, Plano, both of Tex.
[73] **Assignee:** Atlantic Richfield Company, Los Angeles, Calif.
[21] **Appl. No.:** 481,293
[22] **Filed:** Feb. 20, 1990
[31] **Int. Cl.:** E21B 33/138; E21B 33/16
[32] **U.S. Cl.:** 166/291; 166/285; 166/293
[38] **Field of Search:** 166/291, 292, 293, 300, 166/285; 106/90, 314, 315

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Primary Examiner—George A. Seashfield
Attorney, Agent, or Firm—James C. Falk; Arthur F. Zobel; Geoffrey A. Mantooth

[37] **ABSTRACT**
A method of accelerating the set of retarded cement characterized by contacting the retarded cement slurry with a solution containing an effective amount of a compatible accelerator. The compatible accelerator is selected from the group consisting of triethanolamine, diethanolamine and monoethanolamine. This may be employed in overwashing operations, treating retarded cement that is injected into open areas in the well or treating the set of a plug of retarded cement in a well to effect acceleration and/or viscosification of the cement. Also disclosed are specific uses.

9 Claims, No Drawings

4,976,316

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**METHOD OF ACCELERATING SET OF CEMENT
BY WASHOVER FLUID CONTAINING
ALKANOLAMINE**

FIELD OF THE INVENTION

This invention relates to cementing of oil and gas wells. More particularly, this invention relates to accelerating the set of cement that has been retarded to permit safe placement in long duration and long interval cementing operations and those operations where downhole contamination with drilling mud and displacement fluids produces excessive retardation of the cement.

BACKGROUND OF THE INVENTION

Excessive retardation by design is often a problem where wellbore temperature at the top of long liners is inadequate to insure a timely set of cement that has been retarded sufficiently to circulate past the higher wellbore temperatures present at the bottom of the well. Expensive remedial cement squeezes wherein the cement is retarded only enough to insure safe placement at the lower temperature present at the liner lap are typically the only means of insuring a proper cementation and hydraulic seal at the liner lap. An effective means of accelerating the cement set at the liner lap would eliminate the need for expensive remedial cement squeeze operations.

In squeeze cement applications it is desirable to set a retarded cement into open perforations and other void areas within the annular cement sheath or the formation to seal-off these formation intervals that are producing water and/or gas. Ideally the cement will set rapidly after placement. However, excessive retardation of the cement set often results from downhole contamination with the highly retarding drilling mud that may be present during the squeeze operation. The organic polymers and borates common to the fluids used to effect displacement or flushing of any excess cement from the wellbore at the end of some squeeze operations also create excessive retardation of the cement remaining in perforations or other squeezed areas. The risk of cement failure is increased by the longer set time as the cement remains vulnerable to flowback, gas or fluid-out, and dislodgement until time of set. The 4-14 day WOC (Waiting-On-Cement) period that is common to achieve set after a coiled tubing squeeze operation produces additional operational costs. Hydrocarbon production is also lost or deferred during the extended WOC. It is desirable that a compatible accelerator be employed in some fashion to accelerate the set of the cement after placement.

The same is true when placing cement in the form of plugs in the wellbore. This may be for plugging back the well, forming pack-off or seal-off between formations and whipstock or kick-off operations. Cement plugs often fail to set within an allowable time span due to downhole commingling (contamination) with strongly retarding drilling fluids. Commingling results from placement mechanics and gravitational effects. It is desirable that an accelerator be employed to minimize or eliminate the set retarding effects and potential for downhole commingling.

Further, cement often becomes diluted with drilling mud or other downhole fluids due to gravitational exchange. Thixotropic or fast gelling cements are generally acknowledged to reduce this phenomenon, but oper-

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ational and temperature constraints often prevent their use in many cementing operations. It is desirable that a method be available to impart thixotropy or rapid gelation to the cement slurry after placement.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide improved composition and method that will increase the set of retarded cement regardless of what operation it is employed in.

In accordance with one aspect of this invention, there is provided a method of accelerating the set of retarded cements by over washing a cement slurry with a solution of a compatible accelerator of triethanolamine, diethanolamine or monoethanolamine in an amount sufficient to impart rapid gelation and decrease the time it takes for the cement to set either in open perforations, fractures or other void areas, or in a plug in a wellbore.

In another aspect, this invention provides a method of treating a well in which the subterranean formation about the well may or may not be fractured and a low viscosity, retarded cement slurry is squeezed into any open areas of the well that will accept fluid and in which there is provided the improvement of washing over the cement with a solution of a compatible accelerator in an amount sufficient to accelerate the set of the cement. By compatible accelerators is meant triethanolamine, diethanolamine, or monoethanolamine, alone or together in admixture.

In another aspect of this invention there is provided a method of accelerating a cement plug in a well completed in a subterranean formation in which a retarded cement is pumped into the well and allowed to set to form a plug therewithin in which the improvement comprises washing over the cement plug with a solution of a compatible accelerator in an amount sufficient to accelerate the set of the cement.

Additional advantages include counteraction of the cement set retardation effected by in situ intermingling with the drilling fluid. This phenomenon of in situ intermingling is also reduced by the rapid viscification of the cement slurry upon contact with the compatible accelerator.

**DESCRIPTION OF PREFERRED
EMBODIMENTS**

Compatible accelerators in accordance with this invention include amines selected from the group consisting of triethanolamine, diethanolamine and monoethanolamine. These amines, monoethanolamine, diethanolamine or triethanolamine, are described in Hackler's CHEMICAL DICTIONARY, Grant, Editor, Fourth Edition, McGraw Hill Book Company, New York, 1969. As shown therein, even the longest chain triethanolamine is a colorless liquid called trihydroxy triethylamine which boils at 227 degrees Fahrenheit at 150 millimeters mercury pressure. It is soluble in water and is commonly used as a soap base, oil emulsifier and reagent for antimony and tin in pharmaceutical formulations. It is commonly available from any chemical supplier, such as duPont, and does not require extended description herein.

In this invention the compatible accelerator is employed in a proportion or concentration in the range of about 0.1 to 100% by volume as an overwash or spotting fluid. The slug size of the compatible accelerator may be in the same ratio with respect to the cement plug

size. Most preferably, while the concentration may vary slightly from this, it has been found that a slug of the compatible accelerator in the above range will be effective and will result in a setting of cement slurry in only about 24 hours when otherwise it would take from two to nine days for the retarded cement to set.

Other applications in which this is useful is about the same concentration is when an overwash is employed after squeezing cement into perforations and surrounding fractures. As indicated hereinbefore, the cement for such operations is retarded in order to provide adequate safe, pump time for safe placement of the cement into the fractures or perforations. Further, such severely retarded cement may be employed and then washed over with a solution containing the compatible accelerator. The differential pressure from the well out into the formation will probably carry the liquid that is employed as the overwash solution containing the compatible accelerator such as the triethanolamine, diethanolamine or monoethanolamine to the cement plug. Normally such pressure is in the range of 200-300 pounds per square inch (psi) greater in the well than it is in the formation so it tends to effect flushing of the overwash solution containing the compatible accelerator through the cement.

In another operation, the solution containing the accelerator may be spotted ahead of a cement to be placed in a well and the cement then spotted within the column and/or a spot of liquid containing the triethanolamine, diethanolamine or monoethanolamine is positioned above the cement in the well.

A surfactant may be employed in a small concentration of about 0.1-1 percent or so, if desired, to decrease the interfacial tension and help effect the overwash flow through the cement slurry.

Triethanolamine, diethanolamine or monoethanolamine at 0.1-100% is effective for the purpose of this invention. Preferably, a concentration of the compatible accelerator comprising the triethanolamine, diethanolamine or monoethanolamine is in the range of about 5% to 10% by volume of the cement.

The compatible accelerator has the property of accelerating the set of the cement and imparting rapid viscofication or gelation of the cement to minimize gravitational or surge movement of the emplaced cement slurry and has the potential for immediate application for acceleration of cement nodes in remedial squeeze operations, forming cement plugs in a well, or cementing at the top of liners; for example, for whipstock plug operations. Rapid strength development and immobilization of the cement after placement is critical to success in most cementing operations.

The following examples illustrate laboratory experiments performed to simulate field conditions and show effectiveness of triethanolamine, as the compatible accelerator.

EXAMPLE I

In this example, API Class G cement was employed with 1% fluid loss additive in the form of a hydroxy ethylcellulose and a dispersant blend with 0.5% powdered Kellog 32 lignosulfonate retarder and 44% fresh water, giving a cement with a density of 15.9 pounds per gallon. Table I hereinafter illustrates the compressive strength development under curing condition of 190 degrees Fahrenheit and atmospheric pressure.

TABLE I

Sample #	Media (overwash)	@ 24 Hrs.	@ 54 Hrs.	Comments
1	Fresh Water	Not set	2838	Control
2	25% Triethanolamine 75% Fresh Water	1189	3027	
3	25% TEA 5% Sodium Silicate 70% Fresh Water	1084	3081	Precipitate formed in media
4	25% TEA 75% Freshwater	Not Set	3412	

EXAMPLE II

The same cement was made as employed above and cured under the same conditions.

TABLE II

Superadded to media				
Sample #	Media (overwash)	@ 24 Hrs.	@ 41 Hrs.	Comments
2-1	Fresh water	Not Set	45	Control
2-2	20% TEA 80% Fresh Water	1724	2081	
2-3	10% TEA 90% Fresh Water	1894	2411	
2-4	5% TEA 95% Fresh Water	1515	1856	
2-5	10% TEA 3% NaCl (BWOW) 90% Fresh Water	1479	2376	
2-6	10% TEA 3% CaCl ₂ (BWOW) 90% Fresh Water	1579	2611	
2-7	10% TEA 90% Sea Water	1594	2146	

From the foregoing, it can be seen that this invention achieves the objects delineated hereinbefore. More specifically, it provides an accelerator that can be employed to accelerate the set of a retarded cement regardless of where it's used or how it became retarded. This includes avoiding too great a retardation.

Although the invention has been described with a certain degree of particularity, it is understood that the present disclosure is made only by way of example and that numerous changes in the details of construction and the combination and arrangement of steps of the method may be resorted to though departed from the spirit and scope of the invention.

- What is claimed is:
1. A method of treating a well completed into subterranean formations for producing a desired hydrocarbonaceous fluid therefrom which includes the steps of:
setting a packer and squeezing retarded cement into one of open perforations, voids behind the casing and in the formation and any open area of the well-bore, the improvement comprising:
washing over the cement with an overwash comprising a solution of a compatible accelerator selected from the group consisting of triethanolamine, diethanolamine, and monoethanolamine in a concentration sufficient to effect acceleration of the set of the cement slurry compared to the set of the cement slurry without the compatible accelerator.
 2. The method of claim 1 wherein said compatible accelerator is present in a concentration of about 0.1 percent (%) to 100% by volume of overwash fluid.

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3. The method of claim 2 wherein said compatible accelerator is triethanolamine.

4. In a method of setting a cement plug in a well completed in a subterranean formation which a retarded cement is pumped into the well and allowed to set to form a plug therewithin, the improvement comprising: washing over set cement with an overwash comprising solution of a compatible accelerator selected from a group consisting of triethanolamine, diethanolamine and monoethanolamine in a concentration sufficient to effect acceleration of the set of said cement.

5. The method of claim 4 wherein said compatible accelerators present a concentration of about 0.1 to 100% by volume of the overwash fluid.

6. In the method of claim 5 wherein said compatible accelerator is triethanolamine.

7. In a method of accelerating the set of cement at the top of liners within the well in which a retarded cement

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is pumped into the well and allowed to set about top of said liner, improvement comprising:

washing over said cement with a solution of a compatible accelerator selected from the group consisting of triethanolamine, diethanolamine and monoethanolamine in a concentration sufficient to effect acceleration of the set of said cement.

8. In the method of claim 7 wherein said compatible accelerator is triethanolamine.

9. In a method of accelerating the set of cement at the top of liners within the well in which a retarded cement is pumped into the well and allowed to set about top of said liner, improvement comprising:

washing over said cement with a solution of a compatible accelerator selected from the group consisting of triethanolamine, diethanolamine and monoethanolamine in a concentration sufficient to effect acceleration of the set of said cement.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,976,316

DATED : 12-11-90

INVENTOR(S) : Robert B. Carpenter and William N. Wilson

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Please cancel claim 9 and substitute therefor claim
5. (Column 6, line 10)

5. In a method of setting a cement plug in a well completed in a subterranean formation in which a retarded cement is pumped into the well and allowed to set to form a plug therewithin:

the improvement comprising:

injecting a compatible accelerator selected from the group consisting of triethanolamine, diethanolamine and monoethanolamine in a concentration sufficient to effect acceleration of the set of said cement in an area adjacent where the cement is to be placed, followed by said cement to effect in situ mixing with said cement and acceleration of the set of said cement.

Signed and Sealed this

Thirteenth Day of October, 1992

Attest:

DOUGLAS B. COMER

Attesting Officer

Acting Commissioner of Patents and Trademarks

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DS
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United States Patent [19]
Gancy et al.

[11] 4,284,611
[45] Aug. 18, 1981

[54] AQUEOUS PHOSPHATE-STABILIZED
POLYALUMINUM SULFATE SOLUTIONS
AND PREPARATION THEREOF

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[21] Appl. No.: 60,260

[22] Filed: Jan. 25, 1979

[51] Int. Cl.² C01B 25/36

[52] U.S. Cl. 423/308; 210/716;
423/305; 423/309; 423/462; 423/556

[58] Field of Search 423/305, 356, 308, 309,
423/462; 210/716

[56] References Cited

U.S. PATENT DOCUMENTS

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Assistant Examiner—Wayne A. Longel

Attorney, Agent, or Firm—Thomas D. Hoffman

[57] ABSTRACT

A physically and functionally stable solution for water treatment comprises an about 1.2–2.7 molar aqueous phosphate-stabilized polyaluminum sulfate solution of a composition having the formula



wherein

x is about 1.2 to 1.62;
y is about 0.595 to 0.87; and
z is about 0.06 to 0.19

with the proviso that the sum of $x+2y+z$ is 3. The aqueous phosphate-stabilized polyaluminum sulfate solution can be prepared by reacting alumina hydrate with phosphoric acid and contacting the reacted alumina hydrate with an aqueous polyaluminum sulfate solution. Alternatively, the aqueous phosphate-stabilized polyaluminum sulfate solution can be prepared by reacting an aqueous overbasified polyaluminum sulfate phosphate solution with an aqueous aluminum sulfate solution.

15 Claims, No Drawings

95
92

**AQUEOUS PHOSPHATE-STABILIZED
POLYALUMINUM SULFATE SOLUTIONS AND
PREPARATION THEREOF**

DESCRIPTION

1. Field of the Invention

The invention relates to phosphate-stabilized aqueous solutions of polyaluminum sulfate, useful for water treatment; and to processes for their preparation.

2. Background of the Invention

Schmiedel in German Pat. No. 372,246, issued Mar. 26, 1923, teaches that $Al(OH)_3SO_4$ aqueous solutions (8 to 10 weight percent Al_2O_3) are unstable to precipitation but that addition of 0.266 to 0.333 weight percent H_3PO_4 avoids formation of precipitates. Clark et al. in British Pat. No. 443,711, issued Apr. 16, 1936, disclose that in 33-50% basic aluminum sulfate solutions containing 90 grams per liter of alumina, addition of phosphoric acid hinders the precipitation of insoluble basic sulfates. However, the temperatures of 70° C. to 80° C. employed by Clark et al limit the phosphate concentration to a low value. Murata in Japanese Pat. No. 74-40792, published Nov. 5, 1974, discloses a 10% basic polyaluminum sulfate containing 2 weight percent PO_4 and 7 weight percent Al_2O_3 German Pat. Nos. 2 612 503 issued Oct. 21, 1976 and 2 612 504 issued Oct. 21, 1976 disclose basic phosphate and sulfate-containing aluminum chloride solutions.

SUMMARY OF THE INVENTION

In accordance with the present invention aqueous solutions of the following phosphate stabilized polyaluminum sulfate compositions, useful as coagulants in water treatment, have the formula:



wherein

x is about 1.2 to 1.62;

y is about 0.595 to 0.87; and

z is about 0.06 to 0.19

with the proviso that the sum of $x+2y+z$ is 3. Preferably the aqueous solutions are phosphate-stabilized polyaluminum sulfate about 1.2 to 2.7 molar.

The aqueous phosphate-stabilized polyaluminum sulfate solutions are prepared by reacting $Al_2O_3 \cdot nH_2O$ (aluminum hydrate) wherein n is at least about 3 with phosphoric acid, in a ratio of about 3 to 10 moles of H_3PO_4 per mole of $Al_2O_3 \cdot nH_2O$, thereby forming $Al(H_2PO_4)_3 \cdot nH_2O$. The reaction product is then mixed with an aqueous polyaluminum sulfate solution to form the desired aqueous phosphate-stabilized polyaluminum sulfate solution. Alternatively, the product solutions can be prepared by reacting an aqueous overbasic polyaluminum sulfate phosphate solution with aqueous aluminum sulfate (alum) solution. The product solutions can be diluted with water and used as coagulants for water treatment.

**DETAILED DESCRIPTION OF THE
INVENTION**

Generally speaking, the aqueous phosphate-stabilized polyaluminum sulfate solutions of this invention comprise solutions of a composition having the formula:



wherein

x is about 1.2 to 1.62;

y is about 0.595 to 0.87; and

z is about 0.06 to 0.19

with the proviso that the sum $x+2y+z$ is 3.

The aqueous solutions are generally about 1.2 to 2.7 molar.

Preferred solutions are about 1.6 to 1.8 molar and preferably have compositions wherein

x is about 1.3 to 1.34;

y is about 0.76 to 0.8; and

z is about 0.10 to 0.14

with the proviso that the sum $x+2y+z$ is 3.

In one aspect of the present invention, the aqueous phosphate-stabilized polyaluminum sulfate solutions are prepared by reacting $Al_2O_3 \cdot nH_2O$ (aluminum hydrate), wherein n is at least about 3 with phosphoric acid, in a ratio of about 3 to 10 moles of H_3PO_4 per mole of $Al_2O_3 \cdot nH_2O$, thereby forming $Al(H_2PO_4)_3 \cdot nH_2O$. The reaction product is then mixed with an aqueous polyaluminum sulfate solution to form the desired aqueous phosphate-stabilized polyaluminum sulfate solution.

Aqueous polyaluminum sulfate solutions, suitable for treatment with $Al(H_2PO_4)_3 \cdot nH_2O$ to form the compositions of this invention, are obtainable by conventional processes. For example, such process can be based on reaction of aluminum sulfate solution with ground calcium carbonate followed by filtration to separate the precipitated gypsum formed.

Alternative processes for preparing the polyaluminum sulfate solutions include boiling the pure normal alum solution with freshly precipitated aluminum hydroxide and also dissolving natural minerals such as alumite $Al_2(OH)_4SO_4 \cdot 7H_2O$.

Alternatively, the aqueous phosphate-stabilized polyaluminum sulfate solution may be prepared by reacting an aqueous phosphate-stabilized overbasic polyaluminum sulfate phosphate solution with an aqueous alum solution. The basicity of a phosphate stabilized polyaluminum sulfate solution is defined as $(100a/3)$. An overbasic solution is a solution having a higher basicity than the basicity desired in the product.

The desired intermediate basicity (35-45%) aqueous phosphate polyaluminum sulfate solution may be produced directly from phosphate containing alum solution and $CaCO_3$. Alternatively, an aqueous phosphate-stabilized overbasic polyaluminum sulfate solution can be produced, and then blended with the aluminum sulfate hydrate raw material to produce the desired product. In spite of economies of scale the latter route is industrially preferable both in terms of required net realizations, and of fixed capital requirements.

Preferably such solutions are gently heated to a temperature between about 30° C. and 70° C. and then cooled or they are aged at room temperature for at least one day and preferably from about 2 days to 10 days.

The physical stability of the aqueous phosphate-stabilized polyaluminum sulfate solutions is a function of solution basicity, phosphate level, and concentration. At very high concentrations of aluminum, solutions are unstable. It has been found that at low concentrations stability can also suffer, possibly caused by increased hydrolysis of aluminum complexes. It was surprisingly found that aging does not decrease stability of aqueous phosphate-stabilized polyaluminum sulfate solutions. A freshly prepared solution is as stable as a solution when held at 40° C. for 7 days.

The stable aqueous phosphate-stabilized polyaluminum sulfate solution, containing an equivalent of 10 weight percent Al_2O_3 , of the present invention can be blended with alum or $AlCl_3$ to form a superior coagulant.

The solutions of the present invention can be used as a potable water coagulant and as a municipal wastewater coagulant. The solutions of the present invention can be applied to de-watering municipal wastewater and industrial wastewater sludges.

The coagulation properties of the compositions of the present invention remain stable with time and at high levels.

The chloride free solutions of the present invention are in many situations less corrosive than polyaluminum chloride solutions, both in storage, use and in manufacture.

Mol for mol, the aqueous phosphate stabilized basic polyaluminum sulfate solution is a far better coagulant than alum. Reduced dosage requirements of 30% are commonplace. In some natural waters reductions of 50% have been experienced. This means, among other things, reduced volumes of aluminum derived sludges in water treatment plants.

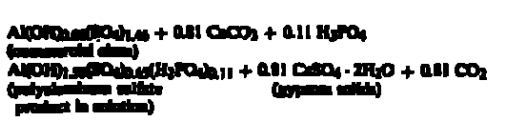
The aqueous phosphate stabilized basic polyaluminum sulfate solution is closely comparable in its effectiveness to polyaluminum chloride solution. A 45% basicity polyaluminum sulfate is comparable to a 70% basicity polyaluminum chloride while lower basicity polyaluminum chloride is not effective. Furthermore, overdosing of polyaluminum chloride in low alkalinity waters can reverse the clarification function. Aqueous phosphate-stabilized basic polyaluminum sulfate solution does not suffer this disadvantage.

EXAMPLE 1

This example illustrates the preparation of a physically stable aqueous phosphate-stabilized high basicity polyaluminum sulfate solution, as well as the preparation therefrom of blends with ordinary aluminum sulfate (commercial "alum") thereby forming a series of lower basic, high performance polyaluminum sulfate compositions.

I. Preparation of Stable Aqueous Phosphate-Stabilized High Basicity Polyaluminum Sulfate

A convenient synthesis was based on the reaction of aluminum sulfate with ground calcium carbonate in the presence of phosphoric acid as represented by the equation below:



200.0 grams of commercial "dry alum" containing 17.1% Al_2O_3 with 2.7% basicity, and 8.5 grams of 85.2% H_3PO_4 , were added to 187 grams of water in a Waring Blender. The mixture was stirred at a slow speed until as much as possible of the alum had dissolved. The degree of agitation was then increased to near maximum level and 34.8 grams of powdered calcium carbonate (99.2% $CaCO_3$) added a little at a time over a period of about 15 minutes. After all the $CaCO_3$ had been added, stirring was continued until the temperature of the resulting polyaluminum sulfate/gypsum slurry rose to about 40° C. and CO_2 evolution had

ceased. The weight of the reaction mixture was adjusted to 425 grams by addition of a small amount of water as required. The gypsum solids were separated by filtration, yielding 280 grams of clear aqueous phosphate-stabilized polyaluminum sulfate product solution.

Analysis of the product solution indicated:
10.29% Al_2O_3 , 12.58% SO_4 , 2.05% PO_4 by weight corresponding to a 53% phosphate-stabilized polyaluminum sulfate of the composition:



The product was heat treated in a rotating sealed container at 60° C. for one hour.

II. Physical Stability of the Aqueous Phosphate-Stabilized Polyaluminum Sulfate Product Solution

The physical stability of the aqueous phosphate-stabilized basic polyaluminum sulfate product solution prepared as above was evaluated by (a) a dynamic test involving pumping and handling designed to simulate operations likely to be encountered in commercial transportation and use, and (b) a specially designed response to a seeding test described below.

II-A. Physical Stability Test Based on Seeding

This test was based on the response of the aqueous phosphate-stabilized basic polyaluminum sulfate solution to seeding by a specific crystalline basic aluminum sulfate which was found to be characteristic of the solid phase which deposits from metastable polyaluminum sulfate solutions on self-destabilization over a wide range of basicities (>25%). The seed had the composition $5 Al_2O_3 \cdot 68 SO_3 \cdot 24 H_2O$ with a well-defined x-ray diffraction pattern and hydrated rapidly in aqueous polyaluminum sulfate to the 40 hydrate, a compound characterized by Bassett and Goodwin (J. Chem. Soc. 1949, page 2248). The response to the seed was monitored by periodic turbidity measurements of the continuously rotated sample following inoculation as described below:

Approximately 20 ml of the aqueous phosphate-stabilized polyaluminum sulfate sample were transferred into a clear glass serum ampule whose cylindrical portion was 7.5 cm in length and 2.0 cm in diameter. Approximately 2 milligrams of the basic aluminum sulfate seed crystal, ground to -325 mesh, was introduced into the aqueous phosphate-stabilized polyaluminum sulfate solution and the ampule sealed with a tight-fitting rubber closure (or flamesealed). The seed was dispersed throughout the sample by manual shaking and an initial turbidity measured by a suitable instrument, e.g. the Hach Model 2100A nephelometer. The ampule was then subjected to a continuous cyclic up-ending as by attachment to the wheel of a ColeParmer Model 7637 Rotator.

Periodic turbidity measurements were recorded daily or more frequently for samples obviously destabilizing rapidly.

The above test was used for the evaluation of various aqueous phosphate-stabilized polyaluminum sulfate solutions, some of which were prepared from reagent alum and others from commercial alum. The former were colorless, while the latter had a light-brown color attributable to certain associated impurities or combinations thereof (e.g. iron and organic matter). It was ob-

5 served during seeding tests that the color of the commercial preparations significantly reduced the turbidity readings compared with comparable reagent counterpart compositions with visually identical turbidities. This precluded direct comparisons of commercial and reagent turbidity data.

Table 1 below presents the seed response data obtained for the aqueous phosphate-stabilized polyaluminum sulfate solution prepared as in I above.

TABLE 1

	Turbidity, FTU*	
	Measured Value	Incremental Turbidity Induced by Seeding
Sample before seeding	3.0	—
Sample immediately after seeding	3.4	0.0
Sample 1 day after seeding	3.8	0.3
Sample 3 days after seeding	4.2	0.6
Sample 6 days after seeding	4.6	1.0
Sample 10 days after seeding	5.0	1.4
Sample 14 days after seeding	5.4	1.8
Sample 16 days after seeding	5.8	2.0
Sample 20 days after seeding	6.2	2.6
Sample 30 days after seeding	6.5	2.9

*Fessenden turbidity scale

These data indicated a very slow response to seeding and thereby confirmed the results of a dynamic stability test mentioned above which indicated a high degree of physical stability for aqueous phosphate-stabilized polyaluminum sulfate solutions of this composition.

III. Preparation of Other Polyaluminum Sulfate Compositions from Aqueous Phosphate-Stabilized High Basicity Polyaluminum Sulfate Solutions By

6 the physical stability. The effect of Al₂O₃ concentration and PO₄/Al ratio on physical stability is shown in Table 4.

A commercial alum liquor containing 8.26% Al₂O₃ was mixed with an equal weight of water.

Aqueous phosphate-stabilized polyaluminum sulfate solution from I. was blended with various proportions of the diluted alum liquor to produce the aqueous phosphate-stabilized polyaluminum sulfate solution compositions shown in Table 3. The aqueous phosphate-stabilized polyaluminum sulfate solution was added dropwise to the vigorously stirred alum solution in all cases.

TABLE 3

Blend	1	2	3	4	5	6
Parts by weight aqueous phosphate-stabilized polyaluminum sulfate from I.	100.0	100.0	100.0	100.0	100.0	100.0
Parts by weight diluted alum	172.6	136.6	111.2	86.2	65.4	46.6
% Basicity	32.5	33.0	37.5	40.0	42.5	45.0
% Al ₂ O ₃	6.39	6.70	7.25	7.43	7.85	8.33
% PO ₄ (on 10 weight percent Al ₂ O ₃ basis)	1.14	1.24	1.33	1.44	1.54	1.63

The blends were evaluated for physical stability and coagulation performance.

IV. Physical Stability and Coagulation Performance of PAS Compositions Formulated by Blending

IV-A Physical Stability

Data covering the response to seeding by the test outlined above in II-A are presented in Table 4 below

TABLE 4

SEED RESPONSE OF AQUEOUS PHOSPHATE-STABILIZED POLYALUMINUM SULFATE SOLUTION/ALUM BLENDS

Blend	Turbidity (F.T.U.)											
	1		2		3		4		5		6	
	A	B	A	B	A	B	A	B	A	B	A	B
Immediately after seeding	1.4	0.0	1.2	0.0	1.6	0.0	1.3	0.0	1.2	0.0	1.4	0.0
1 day after seeding	4.7	1.3	5.0	1.8	6.2	2.6	6.5	3.2	7.5	4.3	6.7	3.3
2 days after seeding	5.7	2.3	6.2	3.0	7.2	3.6	8.2	4.0	8.9	5.7	8.1	4.7
3 days after seeding	6.2	2.8	7.0	3.8	7.7	4.1	8.3	5.0	10.2	7.0	8.4	5.0
7 days after seeding	6.8	3.4	7.5	4.3	8.6	5.0	9.0	5.7	10.8	7.6	8.8	4.4

A - Measured value of turbidity.
B - Incremental turbidity induced by seeding.

Reacting with Alum

Although the aqueous phosphate-stabilized polyaluminum sulfate solution prepared as described in I above exhibits adequate physical stability, its performance as a coagulant was not significantly better than ordinary alum. However, this aqueous phosphate-stabilized polyaluminum sulfate can readily be blended with ordinary alum (which can be considered as zero or low basicity polyaluminum sulfate) to form aqueous phosphate-stabilized polyaluminum sulfate compositions of lower basicity and higher performance.

The first series of aqueous phosphate-stabilized polyaluminum sulfate solution compositions thus prepared were made by blending the aqueous phosphate-stabilized polyaluminum sulfate solution of I. with alum liquor (8.26% Al₂O₃) and water to form a series ranging from about 6 to 8% Al₂O₃ and 32 to 45% basic. The water was included to hold down the Al₂O₃ concentration and help offset the resulting reduced phosphate/aluminum ratio of the blends, which could effect

TABLE 5

COAGULATION PERFORMANCE OF AQUEOUS PHOSPHATE-STABILIZED POLYALUMINUM SULFATE SOLUTION/ALUM BLENDS DESCRIBED IN TABLE 3

Blend	1	2	3	4	5	6
I. WATER TEMPERATURE 68° F.						
Residual Turbidity:						
Blend as Prepared	12	12	13	12	13	11
Blend Aged 1 Day at Room Temp.	10	9.2	9	8.4	9	9
Blend Heat Treated 60° C./1 Hr. After Aging 1 Day at Room Temp.	8	7.6	7.4	6.8	7.3	7
Alum (reference)	14					

II. WATER TEMPERATURE 11° F.

Blend as Prepared	11.5	10.5	12.3	11.5	11.5	11.0
Blend Aged 1 Day						

TABLE 5-continued

COAGULATION PERFORMANCE OF AQUEOUS PHOSPHATE-STABILIZED POLYALUMINUM SULFATE SOLUTION/ALUM BLENDS DESCRIBED IN TABLE 1						
Blend	1	2	3	4	5	6
at Room Temp.	9.4	8.8	8.8	8.0	8.2	8.2
Blend Heat Treated 60° C./1 Hr. After Aging 1 Day at Room Temp.	9.0	8.4	8.4	7.2	7.2	7.6
Alum (reference)	19					

These data show a generally greater response to seeding than that shown by the parent aqueous phosphate-stabilized basic polyaluminum sulfate solution component.

IV-B Coagulation Performance

The coagulation performance of various aqueous phosphate-stabilized polyaluminum sulfate solution compositions were evaluated by two types of coagulation tests:

(a) a selected single dose comparison with alum and Japanese polyaluminum chloride as reference standards, based on the extent of turbidity removal from a turbid water synthesized from tap water and hydraulically fractionated colloidal clay. The test is based on a widely used "jar test" similar to the procedure described in ASTM D 2035. A sample of the turbid water is treated with a measured dose of the coagulant being tested, the water is stirred rapidly, then slowly for specified time periods, and the mixture finally allowed to settle. A sample of the settled water is withdrawn at a specified depth after settling for a specified period, and the residual turbidity measured nephelometrically. The extent to which the original turbidity has been reduced is a measure of the effectiveness of the coagulant.

(b) a relative dosage requirement for an arbitrary degree of turbidity removal (e.g. 90%) compared with alum, determined from dosage curves relating residual turbidity and dosage.

The single dose performance data are presented in Table 5. The data represent the residual turbidity resulting from treatment of a synthetic turbid water (initial turbidity 21 F.T.U., initial pH 8.0) with the quantity of coagulant containing Al₂O₃ equivalent to 6.5 ppm of alum (Al₂(SO₄)₃·14H₂O), at water temperatures of 20° C. and 3° C.

It was observed that the coagulation properties of the blends soon after preparation were poorer than expected from previous data for compositions of these basicities. This was confirmed by the significantly improved coagulation properties following storage of the blends for a single day at ambient temperatures, as presented in Table 5. The one-day old blends were then heat treated at 60° C. for 1 hour, resulting in the further improved coagulation performance values shown in Table 5.

The dosage data are presented in Table 6, and were obtained on a synthetic turbid water with initial turbidity 10 F.T.U., initial pH 8.0. The data indicate that a turbidity removal of 90% (residual turbidity=1.0) required 22.5 ppm of ordinary alum and 17.0 ppm (expressed as equivalent alum) of Blend 3, corresponding to a 25% reduction in coagulant requirement compared to alum.

TABLE 6

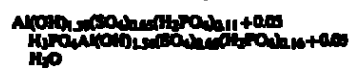
DOSAGE REQUIREMENT DATA - AQUEOUS PHOSPHATE-STABILIZED POLYALUMINUM SULFATE SOLUTION/ALUM BLEND #3 DESCRIBED IN TABLE 1				
Dosage (PPM Alum Equivalent)	6.5	13.0	19.5	26.0
Residual Turbidity:				
Blend 3	4.8	1.6	0.8	0.6
Alum (reference)	11.0	2.3	1.3	0.8

EXAMPLE 2

This example shows the preparation of a second series of blends from a more highly phosphated high basicity polyaluminum sulfate and alum for the purpose of forming lower basic, higher performance polyaluminum sulfate compositions while at the same time providing some extra phosphate to enhance the physical stability of the resulting blends. Note that in Example 1, the reduced PO₄/Al ratio in the blends led to a reduction in physical stability.

I. Preparation of More Highly Phosphated Polyaluminum Sulfate for Use as a Blending Component

The aqueous phosphate-stabilized basic polyaluminum sulfate solution composition in this example was prepared by the simple addition of the appropriate amount of phosphoric acid to the polyaluminum sulfate prepared in previous example, in accordance with the equation:



Analysis indicated the composition to be:

10.16% Al₂O₃, 51.1% Basicity, 3.09% PO₄.

II. Preparation of Other Polyaluminum Sulfate Compositions From Highly Phosphated Polyaluminum Sulfate by Blending with Alum

The aqueous phosphate-stabilized polyaluminum sulfate solution prepared as in I above was blended with various proportions of 1:1 (weight ratio) alum liquor as in the previous Example A. The polyaluminum sulfate compositions thus produced are shown in Table 7.

TABLE 7

Blend	1	2	3	4	5	6
Parts by weight polyaluminum sulfate from I	100.0	100.0	100.0	100.0	100.0	100.0
Parts by weight diluted alum	196.0	124.5	97.5	74.1	51.7	34.8
% Basicity	22.5	33.0	37.3	40.0	42.3	43.0
% Al ₂ O ₃	6.46	6.82	7.18	7.59	8.05	8.57
% PO ₄ (on 10% Al ₂ O ₃ basis)	1.84	1.99	2.16	2.31	2.46	2.63

The phosphate levels with respect to contained aluminum are significantly higher in this series of blends compared with those of Example 1. Each of the blends were split into two portions so that the effect of aging at room temperature and heat treatment on their coagulation properties could be evaluated.

III. Evaluation of Physical Stability and Coagulation Performance

The blends were evaluated by the test procedures outlined in Example 1.

III-A Physical Stability

Data covering the response to seeding are presented in Table 8 below:

TABLE 8 SEED RESPONSE OF AQUEOUS PHOSPHATE-STABILIZED BASIC POLYALUMINUM SULFATE SOLUTION/ALUM BLENDS						
Blend	Turbidity (F.T.U.)					
	1		2		3	
	A	B	A	B	A	B
Immediately after seeding	1.4	0.0	1.6	0.0	1.6	0.0
1 day after seeding	3.9	0.5	4.0	0.4	4.0	0.4
4 days after seeding	4.2	0.8	4.4	0.8	4.3	0.7
7 days after seeding	4.3	0.9	4.6	1.0	4.3	0.7

Blend	4		5		6	
	A	B	A	B	A	B
Immediately after seeding	1.4	0.0	1.6	0.0	1.6	0.0
1 day after seeding	4.1	0.7	4.2	0.4	3.8	0.2
4 days after seeding	4.6	1.2	5.0	1.2	4.0	0.4
7 days after seeding	4.6	1.2	4.8	1.0	4.0	0.4

A - Measured value of turbidity.
B - Incubated turbidity induced by seeding.

TABLE 9 COAGULATION PERFORMANCE OF AQUEOUS PHOSPHATE-STABILIZED BASIC POLYALUMINUM SULFATE SOLUTION/ALUM BLENDS DESCRIBED IN TABLE 7						
Blend	1	2	3	4	5	6
I. WATER TEMPERATURE 20° C.						
Residual Turbidity:						
Blend as Prepared	8.6	1.8	9.0	9.0	8.6	9.0
Blend Aged 1 Day at Room Temp.	8.0	1.0	7.4	8.0	7.1	7.6
Blend Heat Treated 60° C./1Hr. After Aging 1 Day at Room Temp.	7.0	0.4	6.8	6.8	6.0	7.0
Alum (reference)	14					
II. WATER TEMPERATURE 3° C.						
Blend as Prepared	9.2	9.6	9.0	8.6	9.2	10.0
Blend Aged 1 Day at Room Temp.	8.0	2.4	8.0	8.0	7.6	8.0
Blend Heat Treated 60° C./1Hr. After Aging 1 Day at Room Temp.	8.6	9.2	7.4	7.2	7.2	7.6
Alum (reference)	19					

In contrast to the corresponding blends of Example 1, these data indicate a relatively low response to seed, comparable to that, for example, of the highly basic polyaluminum sulfate component used for preparing the blends of Example 1. This attests to the high order of physical stability of the blends of this Example 2, since the physical stability of the aqueous phosphate-stabilized basic polyaluminum sulfate solution component of the previous example was confirmed by the independent dynamic test method described earlier.

III-B Coagulation Performance

The coagulation properties of the blends were evaluated by the test procedures outlined in Example 1.

The single dose performance data are presented in Table 9. The data represent the residual turbidity resulting from treatment of a synthetic turbid water (initial turbidity 21 F.T.U., pH 8.0) with the quantity of coagulant containing Al₂O₃ equivalent to 6.5 ppm of alum, at water temperatures of 20° C. and 3° C.

As for the blends of Example 1, the effect of equilibration, as by storage at room temperature or as accelerated by heat treatment, are stated in Table 9.

The dosage requirements are presented in Table 10 and were obtained on a synthetic turbid water with initial turbidity 5 F.T.U., initial pH 7.0.

TABLE 10 DOSAGE REQUIREMENT OF AQUEOUS PHOSPHATE-STABILIZED POLYALUMINUM SULFATE SOLUTION/ALUM BLEND #3 DESCRIBED IN TABLE 7.				
Dosage (PPM Alum Equivalent)	5	10	15	20
Residual Turbidity:				
Blend 3	2.7	0.7	0.4	0.3
Alum (reference)	3.8	1.0	0.7	0.5
Japanese Polyaluminum Chloride (reference)	1.2	0.5	0.3	0.25

The data indicate that a turbidity removal of 90% (residual turbidity =0.5) required 20.0 ppm of ordinary alum and 13.0 ppm (expressed as equivalent alum) of Blend 3, corresponding to a 35% reduction in coagulant requirement compared to alum.

EXAMPLE 3

This example illustrates the preparation of stable, high performance aqueous phosphate-stabilized polyaluminum sulfate/chloride solutions by blending a phosphated high basicity polyaluminum sulfate with aluminum chloride.

The aqueous phosphate-stabilized polyaluminum sulfate solution used was the aqueous phosphate-stabilized basic polyaluminum sulfate solution product prepared as described in Example 1 under I, namely a 33% basic polyaluminum sulfate containing 10.29% Al₂O₃ and 2.05% PO₄.

Two polyaluminum sulfate/chloride compositions were prepared by blending the aqueous phosphate-stabilized polyaluminum sulfate solution with the appropriate quantities of an aqueous solution of AlCl₃ containing 4.20% Al₂O₃/basicity zero. The aqueous phosphate-stabilized polyaluminum sulfate solution was added dropwise to the stirred AlCl₃ solution in both cases.

Blend 1—35% Basic

100.0 parts by weight of aqueous phosphate-stabilized polyaluminum sulfate solution
124.7 parts by weight of AlCl₃ solution yielding a product of the empirical composition:



containing 6.91% Al₂O₃, 5.60% SO₄, 4.87% Cl, 0.91% PO₄.

Blend 2—45% Basic

100.0 parts by weight of aqueous phosphate-stabilized polyaluminum sulfate solution
42.6 parts by weight of $AlCl_3$ solution yielding a product of the empirical composition:



containing 8.47% Al_2O_3 , 8.82% SO_4 , 2.62% Cl , 1.43% PO_4 .

I. Physical Stability of Aqueous Phosphate-Stabilized Polyaluminum Sulfate Solution/ $AlCl_3$ Blends

The seed response test on Blends 1 and 2 led to the unexpected observation that the seed actually dissolve in these solutions showing the stability of these blends. In contrast, the Taki patent composition responded very strongly to the seed, demonstrating the strong stabilizing effect of phosphate on mixed sulfate/chloride systems.

The seed response data are presented in the Table 11 below:

TABLE 11

	Turbidity P.T.U.		
	Blend 1	Blend 2	Taki Patent Composition*
Before seeding	2.8	2.6	1.5
Immediately after seeding	4.0	3.6	2.5
1 day after seeding	2.8	2.6	170
2 days after seeding	2.8	2.6	700
5 days after seeding	2.8	2.6	>1000
7 days after seeding	2.8	2.6	>1000

*Prepared by adding 40% basic polyaluminum sulfate to $AlCl_3$ solution - product is 37% basic and contains 9.0% Al_2O_3 (contains no phosphate).

II. Coagulation Properties of Aqueous Phosphate-Stabilized Polyaluminum Sulfate Solution/ $AlCl_3$ Blends

The coagulation performance of the blends was evaluated by the single dose method as a function of aging at room temperature and heat treatment at 60° C./1 hour.

The data are presented in Table 12 and represent the residual turbidity resulting from treatment (with a dose corresponding to 6.5 ppm alum equivalent) of a synthetic turbid water whose initial turbidity was 21 P.T.U. and pH 8.0, at two water temperatures (20° C., 3° C.).

TABLE 12

	Residual Turbidity		
	Blend 1 (35% basic)	Blend 2 (45% basic)	Alum
I. Water Temp., 20° C.			
Blend as prepared	10.0	12.0	14.0
Blend after aging 1 day	7.5	8.9	14.0
Blend after aging 2 days	7.3	8.5	14.0
Blend after aging 7 days	7.0	7.2	14.0
Blend after heat treating (60° C./1 hour)	7.3	6.5	14.0
II. Water Temp., 3° C.			
Blend as prepared	7.5	12.4	19.0
Blend after aging 1 day	7.7	10.6	19.0
Blend after aging 2 days	7.3	7.3	19.0
Blend after aging 7 days	7.3	7.0	19.0
Blend after heat treating (60° C./1 hour)	7.0	6.3	19.0

The coagulation data again indicate the effect of aging or heat treating the blends to equilibrate them

structurally and the resulting improvement of their coagulation properties.

We claim:

1. An aqueous chloride-free, phosphate-stabilized polyaluminum sulfate solution, useful as a coagulant in water treatment, having the formula:



wherein

x is about 1.2 to 1.62;
y is about 0.595 to 0.87; and
z is about 0.06 to 0.19,

with the proviso that the sum of $x+2y+z$ is 3.

2. The solution as set forth in claim 1 wherein the solution is about 1.2 to 2.7 molar.

3. The solution as set forth in claim 1 wherein x is about 1.3 to 1.34.

4. The solution as set forth in claim 1 wherein y is about 0.76 to 0.8.

5. The solution as set forth in claim 1 wherein z is about 0.10 to 0.14.

6. The solution as set forth in claim 1 with a turbidity after seeding of less than about 3 Formazin turbidity units for over at least seven days.

7. The solution as set forth in claim 1 having a composition of the formula



8. A process for preparing an aqueous chloride-free, phosphate stabilized polyaluminum sulfate solution, useful as a coagulant in water treatment, having the formula:



wherein

x is about 1.2 to 1.62;
y is about 0.595 to 0.87; and
z is about 0.06 to 0.19,

comprising blending an overbasified aqueous chloride-free phosphate-stabilized polyaluminum sulfate solution with an aqueous chloride-free, alum solution, with the proviso that the sum of $x+2y+z$ is 3.

9. The process as set forth in claim 8 comprising the additional step of heating the solution to a temperature of from about 30° to about 70° C.

10. The process as set forth in claim 8 wherein the solution is allowed to stand for at least 1 day before use as a coagulant.

11. The process as set forth in claim 8 wherein x is about 1.3 to 1.34;
y is about 0.76 to 0.8; and
z is about 0.1 to 0.14.

12. The process as set forth in claim 8 wherein the aqueous phosphate-stabilized polyaluminum sulfate solution is from about 1.6 to about 2.7 molar.

13. A process for preparing an aqueous chloride-free, phosphate-stabilized polyaluminum sulfate solution, useful as a coagulant in water treatment, of a composition having the formula:



wherein

x is about 1.2 to 1.62;
y is about 0.595 to 0.87; and
z is about 0.06 to 0.19

which comprises:

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reacting $Al_2O_3 \cdot nH_2O$, wherein n is at least 3, with chloride-free phosphoric acid, in a ratio of about 3 to 10 moles of H_3PO_4 per mole of $Al_2O_3 \cdot nH_2O$; and mixing the resultant reaction product with an aqueous chloride-free polyaluminum sulfate solution, with the proviso that the sum of $x+2y+Z$ is 3.

14. The process as set forth in claim 9 wherein the aqueous phosphate-stabilized polyaluminum sulfate solution is from about 1.2 to about 2.7 molar.

15. A process for preparing aqueous phosphate-stabilized polyaluminum sulfate/chloride solutions, useful as a coagulant in water treatment, comprising

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blending an aqueous chloride-free phosphate-stabilized polyaluminum sulfate solution of a composition having the formula



wherein

x is about 1.2 to 1.62;

y is about 0.995 to 0.87; and

z is about 0.06 to 0.19

with the proviso that the sum $x+2y+Z$ is 3, with an aqueous aluminum trichloride solution.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,284,611

DATED August 18, 1981

INVENTOR(S) : Alan B. Gancy and Christian A. Wamser

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 37, in the formula: "AL" should read -- A1 --

Col. 3, line 31: "is" should read -- in --

Col. 13, line 7: "8" should read -- 13 --

Col. 14, line 11, in the formula: "7" should read -- z --

Signed and Sealed this

First Day of December 1981

[SEAL]

Attest:

GERALD J. MOSSINGHOFF

Attesting Officer

Commissioner of Patents and Trademarks

27 D6

PATENT SPECIFICATION (1) 1210549

1210549

DRAWINGS ATTACHED

- (21) Application No. 37247/68 (22) Filed 5 Aug. 1968
- (31) Convention Application No. 670 353
- (32) Filed 25 Sept. 1967 in
- (33) United States of America (US)
- (45) Complete Specification published 28 Oct. 1970
- (51) International Classification B 29 d 7/20
- (52) Index at acceptance
H5B 231 340 34Y 412 420 794



(54) PRODUCTION OF EDIBLE TUBULAR COLLAGEN CASING

(71) We, **THE PAT, INC.**, a Corporation organised under the laws of the State of Illinois, United States of America, of 2 North Riverside Plaza, Chicago, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Natural casings are prepared from the intestines of various edible animals, primarily cattle, hogs and sheep. The intestines are removed from the slaughtered animal and are thoroughly cleaned by processes well known in the art. Natural casings, which have been thoroughly cleaned, are stuffed with various sausage meat compositions and formed into sausage links in preparation for cooking. The sausages which are thus formed are cooked by the consumer and the sausage casings eaten with the cooked sausage. In the preparation of certain smoked or pre-cooked sausages, such as frankfurters and the like, the sausage is cooked or smoked or otherwise processed by the meat packer to render it edible without further treatment by the consumer.

Prior to about 1925, substantially all sausage casings were natural casings prepared from animal intestines. Since that time, there have been developed several types of artificial sausage casings, primarily of a regenerated cellulose, which are used in the preparation of the major portion of sausages which are made and sold today. Cellulose casings are used in the preparation of large sausages, such as bolognas, salamis and the like, and are removed from the sausage by the consumer at the time of final preparation for eating. Regenerated cellulose casings are also used in the preparation of frankfurter sausages wherein the casing is stuffed with sausage emulsion, linked, smoked, and cooked, and the casing removed from the finished sausage.

Regenerated cellulose casings have not proved satisfactory for the processing of pork

sausages inasmuch as cellulose is not edible with the sausage and does not transmit the fat which is released from the sausage during cooking. As a result, there has been some demand for an artificial sausage casing which is edible and which has the properties desired in a casing to be used in the processing of pork sausages.

Over a period of many years, artificial sausage casings have been prepared from animal collagen. Casings made of collagen have been prepared by processing animal hide to break the collagen into a fibrous structure and extrude the collagen fibers in the form of a doughy mass to produce tubular casings. The casings which have been prepared in this manner have been hardened with formaldehyde and have been used as a removable casing for processing various sausages. These casings have not been edible even though collagen itself is an edible material. More recently, edible sausage casings of collagen have been prepared and sold in commercial quantities. In the manufacture of edible collagen casings, considerable emphasis has been placed on the necessity for using collagen source materials which have not been subjected to a tanning treatment. In fact, a number of recent patents describing the production of collagen have indicated that it is absolutely necessary to start with an untanned collagen source material if an edible casing is to be obtained. While the use of untanned collagen as a starting material has certain advantages, it has the substantial disadvantage of requiring a more severe mechanical treatment for removal of hair and the epidermal layer from the hides from which the collagen is obtained.

In British patent specification 1,122,504 we described a process in which edible collagen casings are prepared from tanned hide collagen. In that process, animal collagen is obtained from tanned hides which are subsequently subjected to an acid deliming treatment. That process comprises treating a fresh or salt-cured animal hide with a lime-containing solution

[Price 5s. 0d. (25p)]

for a time, in the range 1.5—24 hours, sufficient to at least partially dehair the hide without degrading the collagen, removing the epidermal layer and remaining hair, neutralizing the lime in the hide by treatment at a pH of 2.5—6.5 with a non-toxic acid capable of forming, without swelling the hide, a calcium salt sufficiently soluble to be washable from the hide, and washing to remove by-product salts, grinding the hide at a temperature less than 20°C to produce a slurry of finely-divided collagen in water, treating the slurry with acid at a pH of 2.5—3.7 for a time sufficient to swell the collagen and burst the fiber bundles to form fibrils, extruding the slurry through an annular die to form a collagen tube, immersing the tube in a coagulating bath, tanning the collagen tube, and washing, plasticizing, and drying the tube to produce a translucent non-fibrous edible product.

In the specification of British patent application No. 19008/66, (Serial No. 1,139,233) we described a process for the preparation of edible collagen casings from lined hides which may be subjected to an acid deliming treatment or which may be converted directly into a collagen paste and casings formed without the acid deliming step, provided that the collagen is processed into casing at a sufficiently high speed. That process comprises treating a fresh or frozen or salt-cured animal hide with a lime-containing solution for a time, in the range 3—12 hours, sufficient to at least partially dehair the hide without degrading the collagen, washing the hide to remove excess liming solution, removing the epidermal layer and remaining hair, grinding the limed hide at a temperature less than 20°C to produce a slurry of finely divided collagen in water, treating the slurry with acid at a pH of 2.5—3.7 to swell the collagen and burst the fiber bundles to form fibrils, mild washing, grinding and acidification of the hide being carried out in less than 12 hours, extruding the slurry having a solid collagen content of 2—6% by weight through an annular die to form a collagen tube, immersing the tube in a coagulating bath, tanning the collagen tube, and washing, plasticizing, and drying the tube to produce a translucent nonfibrous edible product.

In the preparation of edible collagen casings, hide collagen is converted into a finely divided fibrillar form and extruded in the form of a dilute collagen slurry (e.g., 2—6% wt. collagen content). The extruded collagen is passed through an annular die into a sodium sulfate and/or ammonium sulfate coagulating bath which dehydrates the collagen slurry and forms a coherent tubular collagen film. At this stage in the processing, however, the salt coagulated collagen tubular film can be handled but will revert to a thin slurry upon further contact with water. It is, therefore,

necessary to harden or tan the extruded collagen tubular film to permit further processing of the tubular film and to provide the tubular film with sufficient strength for use as a sausage casing. A satisfactory tanning process must utilize a tanning agent which is very rapid in tanning action and completely non-toxic in the form in which it is present in the finished casing and must produce a casing of sufficient strength to be stuffed with sausage meat, linked, packaged, and finally cooked. In the preparation of edible collagen casings, one of the most successful methods of hardening or tanning the casing utilizes an alum tanning bath or a bath containing an aluminum salt complex, such as a citrate complex, at a pH suitable for tanning. When casings are tanned or hardened using an aluminum tanning bath, the tanned casing is generally quite strong and easy to handle during processing, reeling, shirring, packaging, etc., but often exhibits certain deficiencies in handling at the time of stuffing with sausage emulsion or during cooking. Aluminum tanned casings generally are somewhat stiff and are difficult to link after stuffing. Also, it has been found that aluminum tanned casings often tend to split during frying of sausages stuffed therein and thus are not entirely satisfactory for the preparation of pork sausages.

In British patent specification 1,122,905 we described a process for tanning or hardening edible collagen casing comprising collagen fibrils which comprises contacting the casing with a solution of an edible non-toxic dialdehyde at a pH of 4.0—7.0 and washing and drying the casing. As the dialdehyde tanning agent, glutaraldehyde may be used. That tanning process is applicable in the preparation of edible collagen casings from either lined or unlined animal hides.

One object of the present invention is to provide a new and improved process of tanning or hardening edible tubular collagen casings prepared from lined or unlined hides.

Another object of this invention is to provide a new and improved tanned or hardened edible tubular collagen casing prepared from lined or unlined hides and having superior stuffing, linking and cooking properties.

A feature of this invention is the provision of a process of tanning an edible extruded tubular collagen casing which comprises passing the extruded casing through an aluminum tanning bath comprising a solution of an aluminum salt complexed with an organic acid capable of forming a stable chelate with aluminum, rendered partially basic and at a concentration sufficient to produce an aluminum content of 1.5—5.0% by weight in the treated casing, washing the casing, and then passing the casing through a glutaraldehyde tanning bath comprising a 0.01—5.0 by weight solution of glutaraldehyde, and wash-

ing, plasticizing and drying the tanned casing so obtained.

Another feature of this invention is the provision of a new and improved edible tubular collagen casing prepared from limed or unlimed animal hide and tanned by a process as above defined, the casing being characterized by improved stuffing, linking, and cooking properties.

In practicing this invention satisfactory edible collagen sausage casings can be prepared using limed or unlimed hides as the source of collagen, and tanned or hardened by the tanning process of this invention to yield a casing having improved stuffing, linking, and cooking properties. The animal hide is treated to remove the blood quickly and is frozen or salt-cured, or immediately treated with a lime-containing solution to at least partially dehair the hide. The liming treatment (of the fresh, frozen, or salt-cured hide) is preferably carried out in less than 48 hours. Alternatively, the hide may be treated with dilute non-toxic acid after liming to remove then reacted calcium from the collagen. The hide is then washed, dehaired, ground at a temperature less than 20°C, and swollen with a non-toxic acid at a pH of 2.5-3.7. These steps are preferably carried out rapidly, viz., in less than 48 hours, more preferably less than 12 hours.

When the hide is limed, washed, ground, and swollen, a slurry is produced which is extruded through an annular die into a coagulating bath, e.g., of sodium sulfate or ammonium sulfate, to form a tubular casing. The casing is then passed through an aluminum tanning solution, washed, and then passed through a glutaraldehyde tanning solution. The tanned casing so obtained is washed and then plasticized, e.g., with a glycerin solution. The tanned, washed, and plasticized casing is then dried, reeled, and eventually skinned and packaged.

The product casing thereby produced performs better in stuffing, linking and cooking than casing prepared by prior art techniques. A similar improvement in casing properties is obtained when collagen slurries prepared from unlimed hides or enzymatically dehaired hides are extruded and coagulated to form tubular casing which is tanned in a tanning process as described above.

This invention will be understood more fully by reference to the following description and the accompanying drawings, in which:

Fig. 1 is a flow diagram illustrating schematically the more important steps in the initial preparation, extrusion, tanning, and processing of edible collagen casings.

Fig. 2 is a schematic view of the equipment used in the more important steps in the preparation of edible collagen casings.

Fig. 3 is extruded edible collagen casing

prepared in accordance with this invention as processed in a skinned form, and

Fig. 4 is a schematic view showing the filling of the casing with sausage meat on an extrusion horn or nozzle, and the preparation of sausage links therefrom.

In a preferred method of preparing edible collagen casings, animal hides, preferably steer or cattle hides, are cut into suitable pieces (hide trimmings may also be used) are treated with a suitable lime solution for removal of hair. The hide may also be limed before cutting into small pieces if desired. The lime solution is preferably a solution containing excess acid lime $[\text{Ca}(\text{OH})_2]$, sodium salt-hydrate (NaSH) and, optionally, dimethyl-amine sulfate $[(\text{CH}_3)_2\text{NH}]_2\text{SO}_4$. After treatment in such a solution for a period of less than two days (3-12 hours or less is preferred), the hides are removed and washed. After washing, the hides are split or otherwise mechanically abraded to remove the epidermal layer and any remaining hair.

The hides which are thus prepared are washed in a solution containing a non-toxic acid, such as an edible grade lactic acid, to clean the hides further and to neutralize excess lime in the hides. This cleaning and neutralization step is preferably carried out in accordance with the procedure described in British patent specification 1,122,504. The hides are then cut into small pieces and ground into particles of very small size to produce an aqueous slurry having a collagen content in the range from 2-6% by weight, preferably about 3.5-5%. The collagen is maintained at a temperature less than 20°C (preferably less than 10°C) during the grinding, by repeated addition of ice to the mixture. The collagen slurry which is thus prepared is treated with the dilute solution of weak acid to swell and burst the collagen fibers as previously described. The washing, dehairing, grinding and acid swelling of the collagen are carried out in a relatively short time, generally less than about 48 hours.

The swollen collagen slurry is then extruded through an annular die to produce a thin-walled tubular product suitable for use as sausage casings after obtain maximum strength in the product casing, the collagen slurry is preferably extruded through a die having rotating inner and/or outer parts which are well-known in the prior art in the preparation of collagen casings, vide U.S. Patent 2,046,541.

The collagen slurry is extruded through the die into a coagulating bath consisting of a concentrated solution of sodium sulfate and/or ammonium sulfate. The thin-walled collagen tube which is formed in the coagulating bath is then passed into a first tanning bath consisting of a solution of an aluminum salt, rendered partially basic or buffered to a pH in excess of 3.0. The casing is next passed

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40 105
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50 115
55 120
60 125
65 130

through a wash bath and then through a second tanning bath consisting of a dilute solution of glutaraldehyde and then washed and plasticized. The casing which is thus prepared is inflated with air or other gas and passed through a dryer from which the casing is rolled up on reels and subsequently shirred. If desired, it is possible to shir the casing directly out of the dryer. This has the advantage that it is easier to maintain the casing in an inflated state, but has the disadvantage that the shirring machine is capable of operation at a substantially higher rate of speed than the rate of extrusion of casing in the process. The casing may be shirred on shirring machines of the type used in the shirring of regenerated cellulose casings, such as those shown in British Patents 764,455 and 993,148.

In Fig. 2 of the drawings, the steps from extrusion through reeling or shirring are illustrated schematically in slightly more detail. The collagen slurry is introduced through inlet conduit 1 into a die 2 having an annular die outlet 3 through which casing 4 is extruded. The die 2 has an inner tube 5 which extends upwardly within the extruded casing to remove coagulating bath from within the extruded casing. Die 2 is preferably a die having a pair of counter rotating members which give the collagen fibers a mixed orientation and thus produce a stronger casing. The die 2 is located at the bottom of container 6 which contains coagulating bath 7 (a concentrated solution of sodium sulfate or ammonium sulfate). Coagulating bath 7 is circulated through conduit 8 from tube 5 for removal of the coagulating bath from inside the extruded casing. Casing 4 which is coagulated in bath 7 passes over a series of rollers and is directed through the first tanning bath 9.

Tanning bath 9 consists of an aqueous solution of an aluminum salt complexed with an organic acid which is capable of forming a chelate with aluminum. The solution is preferably of aluminum sulfate or other aluminum salts which have been treated to produce a complex such as a citric acid or sodium citrate complex, and have been partially neutralized, as with sodium carbonate, to render the salt complex partially basic. The tanning bath is preferably at a pH in excess of 3.0, and is at a concentration sufficient to produce an aluminum content of 1.5—5.0% wt. in the treated casing.

From the tanning bath 9 the casing passes through a wash bath 10 where unreacted tanning reagent is washed out of the casing. The casing is then passed through a second tanning bath 11 which consists of a dilute solution of glutaraldehyde. From the second tanning bath 11 the casing is then passed through a second wash bath 12 which removes unreacted tanning agent. From wash bath 12 the casing passes through plasticizing bath 13 which consists of a solution of glycerin

which may contain a trace of a volatile aldehyde such as formaldehyde or pyruvic aldehyde.

From the plasticizing bath 13, the casing passes through dryer 14 where it is inflated and dried with the air of air circulated by fan or blower 15 through air heater 16. After leaving dryer 14, the casing is preferably rolled up on reel 17 and is eventually shirred on a commercial shirring machine of the type used in the shirring of regenerated cellulose sausage casings as noted above. If desired, the casing may be passed directly to a shirring machine shown diagrammatically as 18.

After the casing is shirred into individual short strands, it is packaged and, optionally, may be cured by heating at 60—80°C in an atmosphere of 20—50% relative humidity for several hours prior to shipment to the meat packer. In Fig. 4, the stuffing of the casing is illustrated. A strand of edible aluminum-glutaraldehyde-treated collagen casing 19 is placed on a tubular stuffing horn 20 which is connected to a pressurized source of sausage emulsion (not shown). The sausage emulsion is passed through the stuffing horn 20 of the end of casing 19 and the casing is filled with sausage meat and twisted at suitable intervals to provide sausage links 21. The links may be severed from each other and packaged in a suitable overwrap following conventional meat packaging techniques. Alternatively, the links may be packaged in an unsevered string. When the sausage is cooked by the consumer, the casing is found to be quite strong and shirtable with the meat during cooking. The casing may be prestock (i.e., provided with minute holes formed in it at the time of manufacture), if desired, to permit more rapid release of fat during the cooking of the sausage. Casing which is prepared in this manner has been found to have a shrinkage temperature which is equal to or greater than native collagen and thus does not shrink excessively during cooking. This casing is easy to form into links, stuffs easily without excessive breakage, and cooks well without excessive splitting.

In this process, the use of glutaraldehyde retanning bath following the aluminum tanning bath has been found to be necessary to produce a casing which links properly and which cooks properly without excessive splitting. When the process described above was carried out with the glutaraldehyde tanning bath omitted, the casing which was produced was of adequate strength for processing, shirring, and packaging, but was found to be extremely difficult to link after stuffing, and the links which were formed were characterized by excessive splitting during cooking. The improvements in casing properties obtained using the combination of aluminum and glutaraldehyde tanning is also obtained when casing is prepared from unfixed hide collagen using the same two-step tanning process.

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The following non-limiting examples are illustrative of the application of this invention to the preparation of a satisfactorily edible collagen casing.

EXAMPLE 1

In this example, the preparation of edible collagen casings from limed animal hides with a combined aluminum-glutaraldehyde tanning is illustrated. Selected cattle hides from carcasses certified fit for human consumption, weighing about 65-75 lbs. each, are the starting material for this process.

As soon as possible after flaying and inspection, the hides are washed in a large volume of circulating cool (10°C) water to remove adhering blood. After washing, the hides are fleshed fresh, without curing, to remove adhering fat and muscular debris from the flaying operation.

The washed and fleshed hides are then treated in a liming bath containing 6% wt. of fresh calcium hydroxide and 1.5% wt. of sodium sulfhydrate (the liming bath may contain up to 5% dimethylamine sulfate), as solution and/or slurry contained in about 450% wt. of water at room temperature (15-20°C), all percentages being calculated on the weight of the hide treated. The treatment is carried out for a period less than about 6 hours, sufficient to remove most of the hair from the hide, and the hides are gently agitated from time to time to insure even penetration of the liming liquor.

After liming, the hides are removed from the liming bath and permitted to drain for a period of 1/2 hour while suspended. The limed hides are then gently squeezed, as between rubber rollers, to remove excess liming liquor.

The hides which have been thus limed, drained and squeezed, are then cut or split in the plane of the hide into two approximately equal portions by weight. The upper or outer hide surface contains all of the hair, hair follicles, sebaceous and sudorific glands. The inner or corium layer consists substantially of collagen. The outer or hair-containing layer or split is discarded as unsuitable for use in the preparation of casing but may be used for formation of leather leathers or coverings.

The corium layer or split is then placed in a tank or vat containing about 4.5 times the hide weight of water at a temperature less than about 15°C. Gentle agitation is used to ensure even removal of debris and adhering lime solution and/or slurry. The hides are washed during a period of 20-30 minutes. The washings are removed and the corium splits resuspended in 4.5 times their weight of cool (15°C) water. Edible grade lactic acid, suitably diluted at a concentration of 2-4 ounces of 44% lactic acid per quart of cool (15°C) water is added in small portions at 15-minute

intervals, with gentle agitation for 5 minutes of each 15-minute period. The liquor is tested for pH before each addition, and the end point is regarded as the point when the pH is permanently depressed below 7.0. In general, this requires about 1.5% wt. of 44% lactic acid, based on the weight of the corium split. This treatment is effective to neutralize the excess lime in the corium layer and to remove it as a soluble salt. The rate of addition of the lactic acid solution is carefully regulated so that the temperature of the bath is never permitted to rise above about 32°C.

The neutralized and delimed corium splits are then removed from the neutralization bath, drained and rinsed in cool (15°C) water, packed into polyethylene bags which are in turn placed in 50-gallon fiber drums. Dry ice in sufficient quantity is placed above and below the polyethylene bags to chill the prepared collagen and to maintain it below 3°C during storage and/or shipment prior to comminution and acid swelling operations prior to extrusion. It should be noted, however, that the hides may, if desired, be cut into small pieces or small pieces of scrap hide material may be used in the steps of liming, splitting, and neutralization or deliming.

The delimed corium splits are cut into small square or rectangular sections, e.g., 1/4 to 4 inches on a side, in preparation for grinding. The small pieces of treated hide are converted to a fine pulp by successive passes through a meat grinder. In this grinding operation, sufficient ice is mixed with the hide splits to maintain the temperature below 20°C (and preferably below about 10°C). Successive passes through the meat grinder use successive smaller dies, the smallest being about 3/64 inch. At this point, sufficient water is added to the pulp to produce a mixture consisting of about 90% wt. water and 10% wt. collagen.

The collagen pulp is then treated with sufficient dilute lactic acid (other dilute or weak acids such as citric or acetic acid may be used) to produce a pH of 2.5-3.7. The acid is usually added as a dilute solution e.g., 0.8-2.0% wt. After thorough mixing, the pulp and acid are stored overnight at a temperature of about 3°C to swell. At the end of this time the collagen is swollen and has taken up all of the water in the mixture. The swollen collagen is mixed with sufficient water and acid to maintain the pH of 2.5-3.7, thus producing a swollen collagen slurry as a thin homogeneous paste containing 4% wt. collagen and 1.2% wt. lactic acid.

The swollen collagen slurry is passed through a homogenizer to further disperse the fibers and then is filtered to remove any undispersed fiber clumps or other solid contaminants. The paste is generally deaerated by storage under vacuum prior to extrusion. The process, from the washing of the limed hide through the acid swelling of the comminuted collagen, is

preferably carried out in a period of 6-12 hours (and generally no longer than 48 hours).

3 The homogenized and filtered collagen slurry is then pumped under pressure through the extrusion die as previously described, into a coagulating bath consisting of about 40% wt. ammonium sulfate (sodium sulfate can also be used) in water. When the collagen is extruded as a thin-walled tube into this concentration of ammonium sulfate, the collagen fibrils are dehydrated and collapse to form a film which is sufficiently coherent for further processing. As shown in Fig. 2 of the drawings, the coagulation bath is circulated both inside and outside the tube to maintain the tube in an inflated condition and to insure proper coagulation of the casing both on the inside and outside.

10 After the film is coagulated in the ammonium sulfate solution, it is necessary to tan the film to give the film sufficient strength for further processing and for stuffing with sausage meat. If the film were taken from the ammonium sulfate coagulating bath and were dried, a film would be produced which has moderate strength in the dry state but which would revert to a paste upon contact with water. It is, therefore, necessary for the casing to be tanned or hardened to provide the wet and dry strength in a finished product required in an edible casing.

15 From the coagulation bath, the casing next passes into a first tanning bath which comprises a solution containing 10-20% wt. of aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, 3-7% wt. sodium citrate (or an equivalent amount of citric acid) and 3-7% wt. sodium carbonate. The tanning bath is formulated so that the sodium citrate or citric acid forms a complex with the aluminum sulfate, and the sodium carbonate neutralizes a portion of the aluminum-citrate complex to render the same about one-third to two-thirds basic. This results in a tanning bath having a pH above 3.0 and permits the use of aluminum concentrates for tanning which are many times the concentrations available with other aluminum tanning baths, such as alum tanning baths, and are of sufficient concentration to produce an aluminum content of from 1.5-5.0% wt. in the casing.

20 From the first hardening bath or tanning bath, the casing passes through a wash bath, as previously described, in which unreacted tanning or hardening reagent is washed out of the casing. The casing is then passed through a second hardening bath consisting of 0.15% wt. solution of glutaraldehyde in water. Glutaraldehyde solutions ranging from 0.01-5.0% wt. concentration may be used, depending upon the residence time of the casing in the solution and the temperature of the treating solution, and the amount of washing to which the casing is subjected.

25 Following the treatment with glutaraldehyde solution, the casing passes into an additional wash bath (or baths) to wash out unreacted tanning or hardening reagents. The casing is then passed through a plasticizing bath consisting of an aqueous solution of glycerin (or equivalent plasticizer such as sorbitol, di-propylene glycol, triethylene glycol, and the like). The plasticizing bath introduces a substantial amount of the desired plasticizer into the casing, which prevents it from becoming hard and brittle after drying.

70 From the plasticizing bath, the casing passes through a dryer where it is inflated and dried with the aid of heated air circulated by a fan or blower as described above. Upon leaving the dryer, the casing is partially rehumidified, rolled up on reels, and then shirred on a machine similar to the type used in the shirring of regenerated cellulose casings. Alternatively, the casing may be shirred directly out of the dryer. After the casing is shirred into individual short lengths, it is packaged in suitable cartons. Optionally, the casing may be cured after packaging by heating at about 80°C in an atmosphere of 20-50% relative humidity for several hours prior to shipment to the meat packer.

80 The composition by weight of the final product casing is approximately as follows:

Collagen	74%	95
Glycerin	14%	
Water	9%	
Aluminum	2%	
Fat	1%	
Total	100%	100

105 The several washing steps in this process are effective to remove essentially all of the reagents used in tanning the hides and in hardening or tanning of the extruded casing, with the exception of a minor amount of calcium (less than about 0.5% wt.) and aluminum (about 2% wt.) which is chemically bound in the collagen. The aldehyde treatments do not leave any residue of free aldehyde. The casing has been analyzed with Schiff's reagent and no free aldehyde is found. The casing has been thermally decomposed and no formaldehyde was found. Also, the casing was hydrolyzed and completely digested with 6M hydrochloric acid, and steam distilled, and no formaldehyde was found. The casing was analyzed for sulfides and none were found.

110 When this casing was used by the meat packer in a shirred form as illustrated in Fig. 3 and stuffed with sausage meat and formed into links as shown in Fig. 4, a satisfactory sausage product was obtained. The casing was found to function well in stuffing and was formed easily by the linking machine into the desired sausage links. When the sausages were cooked the casing was found to shrink with the meat and to release fat cooked out. There

65

was no excessive tendency of the casing to split during cooking.

EXAMPLE 2

5 In this example, frozen steer hides are substituted for fresh cattle hides in the process. The frozen steer hides are thawed and limed as described in the previous example. All other processing steps are as described in Example 1. The casing which is produced is a commercially acceptable casing which is easily handled during processing and stuffing, linking and cooking.

EXAMPLE 3

15 A series of experiments were carried out in which the procedure was varied by omitting the second tanning step and/or omitting the trace of aldehyde in the plasticizing bath.

20 In a series of experiments, the casing was prepared as described in Example 1 except for the omission of the glutaraldehyde tanning step. In these experiments, the casing was passed directly from the wash bath following the aluminum tanning bath to the plasticizing bath and then into the dryer. The casing which was produced was of a strength approximately equal to that obtained in Example 1. The casing shirred well and was packaged and handled by the meat packer easily. The casing was stuffed easily but did not perform satisfactorily in the linker. The elastic properties of the casing did not appear to be adequate to link properly. When the casing was twisted by the linker, it did not take a permanent set and tended to unwind and form long masses of sausage rather than separate links as desired. Several experiments were carried out in the preparation of the casing in which the concentration of aluminum salts in the tanning bath and the residence time of the casing in the tanning bath were varied in an attempt to produce an acceptable casing which could be linked. These experiments were largely unsuccessful. Generally, the casing prepared by use of the aluminum tanning bath alone, without the subsequent treatment with a dilute glutaraldehyde solution, produces a casing which is extremely difficult to link. Even where it was possible to form adequate links in the stuffed casing, the incidence of splitting of the casing during cooking of the sausage links was much higher than was the case for casing which had been given the supplemental glutaraldehyde tanning.

EXAMPLE 4

60 The improvement in stuffing, linking and cooking properties obtained by the sequential tanning of collagen casing was aluminum and glutaraldehyde is also obtained when such a tanning process is applied to the treatment of casing prepared from unlimed collagen. Selected steer hides from carcasses fit for

human consumption, weighing about 65-75 lbs. each, are the starting material for this process. As soon as possible after flaying and inspection, the hides are washed in a large volume of circulating cool (10°C) water to remove adhering blood. After washing, the hides are fleshed fresh without curing to remove adhering fatty or muscular debris from the flaying operation.

70 The washed and fleshed hides are then treated in dilute acetic acid for several days to partially swell the hide and loosen the hair. After the acetic acid treatment, the hides are split or cut in the plane of the hide into two approximately equal portions by weight. The upper or outer hide surface contains all of the hair, hair follicles, sebaceous and sudorific glands. The inner or corium layer consists substantially of collagen. The outer or hair-containing layer or split is discarded as unsuitable for use in the preparation of casing, but may be used for the formation of leather laminates or coverings.

80 The corium split is then neutralized in a dilute solution of sodium bicarbonate. The hides are then washed and cut into small sections as described in Example 1. The pieces of corium splits are then converted into a fine pulp by successive passes through a meat grinder. The pulp is treated with lactic acid as described in Example 1, to cause it to swell to prepare a slurry suitable for extrusion. The slurry is then homogenized and filtered and extruded, tanned, plasticized, dried, reeled and shirred, as described in Example 1.

90 The casing which is obtained in this manner by a two step, aluminum-glutaraldehyde tanning has improved stuffing, linking and cooking properties as described for the casing produced in accordance with Example 1.

WHAT WE CLAIM IS:--

105 1. A process of tanning an edible extruded tubular collagen casing which comprises passing the extruded casing through an aluminum tanning bath comprising a solution of an aluminum salt complexed with an organic acid capable of forming a stable chelate with aluminum, rendered partially basic and at a concentration sufficient to produce an aluminum content of 1.5-5.0% by weight in the treated casing, washing the casing, and then passing the casing through a glutaraldehyde tanning bath comprising a 0.01-5.0% by weight solution of glutaraldehyde, and washing plasticizing and drying the tanned casing so obtained.

120 2. A process in accordance with claim 1 in which the aluminum tanning bath has a pH in excess of 3.0.

125 3. A process in accordance with claim 1 or 2 in which the aluminum tanning bath comprises a solution of 10-20% by weight aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, 3-7% by weight sodium citrate, and 3-7% by

weight sodium carbonate, formulated to produce a one-third to two-thirds basic aluminum sulfate salt complexed with sodium citrate.

5 4. A process in accordance with claim 1 substantially as hereinbefore described with reference to and as illustrated in Figs. 1 and 2 of the accompanying drawings.

10 5. A process in accordance with claim 1 substantially as described in any one of the foregoing Examples 1, 2 and 4.

6. An edible tubular collagen casing prepared by a process in accordance with any one of claims 1 to 5.

7. An edible tubular collagen casing as claimed in claim 6 in a stirred condition.

8. An edible sausage comprising an edible tubular collagen casing as claimed in claim 6 stuffed with a sausage meat.

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FIG. 1

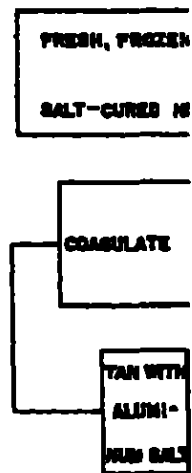
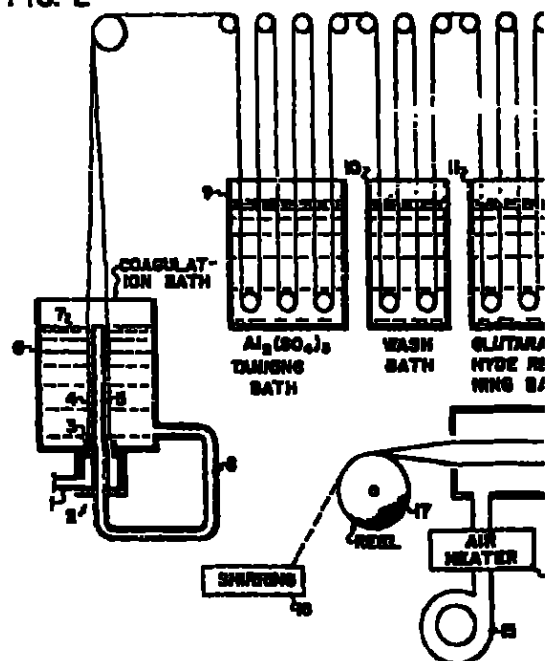


FIG. 2



HZ 109

1210549 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of the Original on a reduced scale

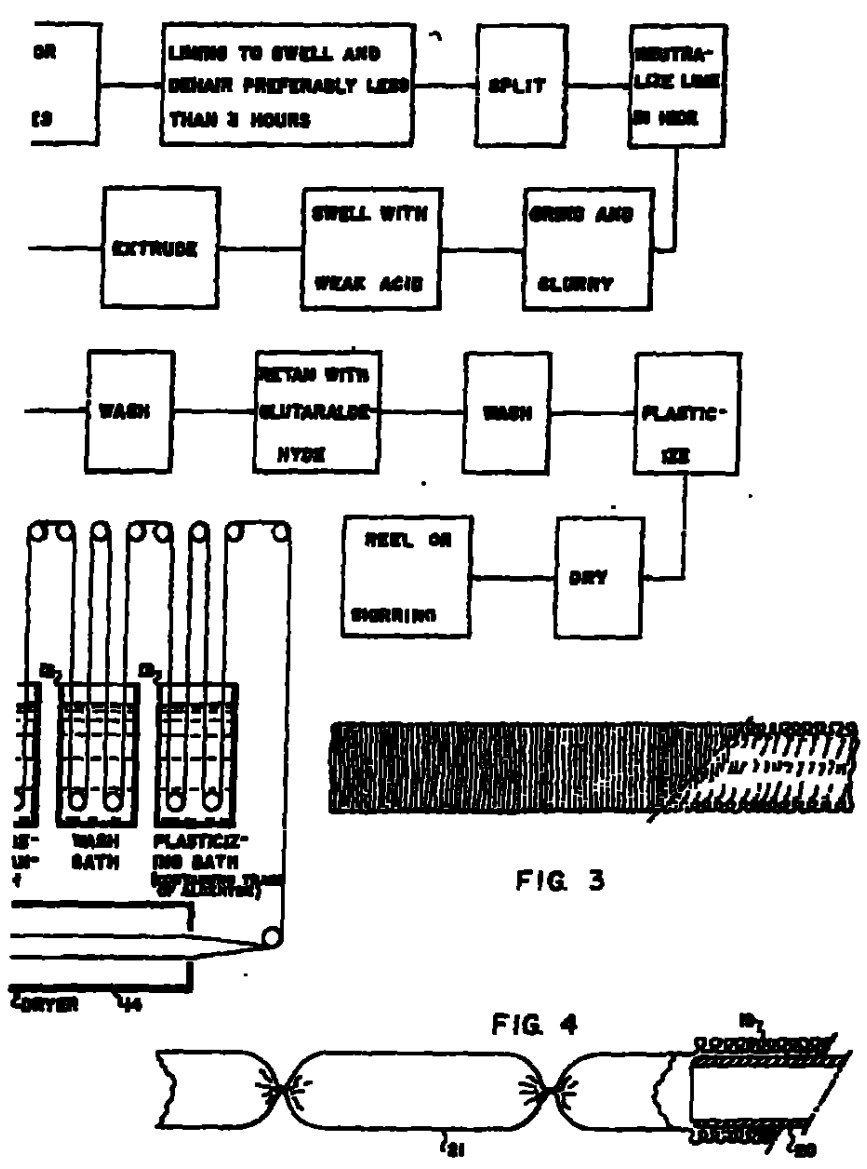


FIG. 1

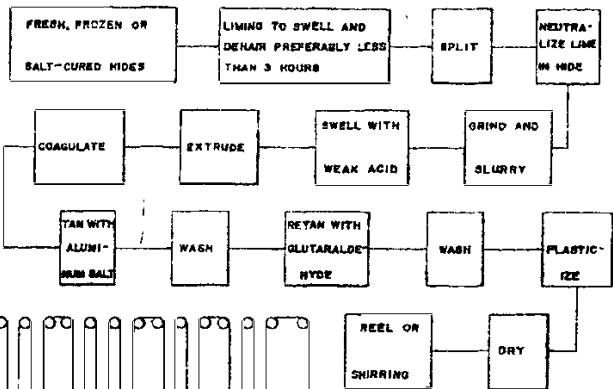


FIG. 2

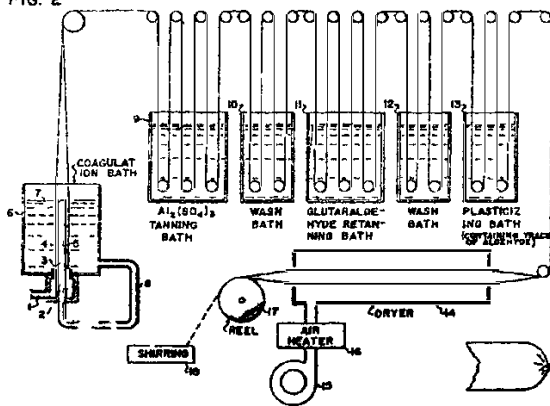
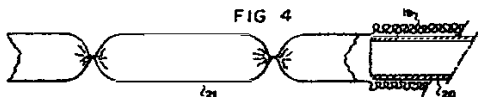


FIG 3



FIG 4



Fichas Internacionales de Seguridad Química

SULFATO DE ALUMINIO

ICSC: 1191

SULFATO DE ALUMINIO

Sulfato aluminico

Trisulfato de aluminio

$Al_2S_3O_{12}/Al_2(SO_4)_3$

Masa molecular: 342.14

Nº CAS 10043-01-3

Nº RTECS BD1700000

Nº ICSC 1191

TIPOS DE PELIGRO/ EXPOSICION	PELIGROS/ SINTOMAS AGUDOS	PREVENCION	PRIMEROS AUXILIOS/ LUCHA CONTRA INCENDIOS
INCENDIO	No combustible. En caso de incendio se desprenden humos (o gases) tóxicos e irritantes.		En caso de incendio en el entorno: están permitidos todos los agentes extintores.
EXPLOSION			En caso de incendio: mantener fríos los bidones y demás instalaciones rociando con agua.
EXPOSICION		¡EVITAR LA DISPERSION DEL POLVO! ¡HIGIENE Estricta!	
• INHALACION	Tos, jadeo, dolor de garganta.	Evitar la inhalación de polvo fino y niebla. Extracción localizada o protección respiratoria.	Aire limpio, reposo y proporcionar asistencia médica.
• PIEL	Enrojecimiento, dolor.	Gautes protectores y traje de protección.	Aclarar la piel con agua abundante o ducharse y proporcionar asistencia médica.
• OJOS	Enrojecimiento, quemaduras profundas graves.	Gafas ajustadas de seguridad.	Enjuagar con agua abundante durante varios minutos (quitar las lentes de contacto si puede hacerse con facilidad) y proporcionar asistencia médica.
• INGESTION	Dolor abdominal, sensación de quemazón, náuseas, vómitos.	No comer, ni beber, ni fumar durante el trabajo.	Enjuagar la boca. NO provocar el vómito. Dar a beber agua abundante y proporcionar asistencia médica.

DERRAMAS Y FUGAS	ALMACENAMIENTO	ENVASADO Y ETIQUETADO
Barrer la sustancia derramada e introducirla en un recipiente; si fuera necesario, humedecer el polvo para evitar su dispersión. (Protección personal adicional: respirador de filtro P2 contra partículas nocivas).	Separado de bases fuertes. Mantener en lugar seco.	Clasificación de Peligros NU: 9.2 Grupo de Envasado NU: III

VEASE AL DORSO INFORMACION IMPORTANTE

ICSC: 1191

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SULFATO DE ALUMINIO

ICSC: 1191

D	ESTADO FISICO; ASPECTO	VIAS DE EXPOSICION
A	Polvo o cristales blanco brillantes. Inodoros.	La sustancia se puede absorber por inhalación y por ingestión.
T	PELIGROS FISICOS	
O	PELIGROS QUIMICOS	RIESGO DE INHALACION
S	La sustancia se descompone al calentarse intensamente o al arder, produciendo humos tóxicos y corrosivos, incluyendo óxidos de azufre. La disolución en agua es moderadamente ácida. Reacciona con álcalis. Ataca a muchos metales en presencia de agua.	La evaporación a 20°C es despreciable; sin embargo, se puede alcanzar rápidamente una concentración nociva de partículas en el aire cuando se dispersa, especialmente si está en forma de polvo.
I		EFFECTOS DE EXPOSICION DE CORTA DURACION
M	LIMITES DE EXPOSICION	La sustancia irrita los ojos, la piel y el tracto respiratorio. Corrosiva por ingestión.
P	TLV (como TWA): 2 mg/m³ (como Al, sales solubles) (ACGIH 1998).	EFFECTOS DE EXPOSICION PROLONGADA O REPETIDA
O		

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112

R T A N T E S	
PROPIEDADES FÍSICAS	Punto de fusión (se descompone): 770°C Solubilidad en agua: Elevada. Densidad relativa (agua = 1): 2.71
DATOS AMBIENTALES	Esta sustancia puede ser peligrosa para el ambiente; debería prestarse atención especial a los peces. 
NOTAS	
Alumbre, Alumbre de perla, alumbre en masa, alumbre de los papeleros, alumbre de filtro son otros nombres con el que se conoce al sulfato de aluminio. Se encuentra en la naturaleza en forma de mineral de alúgonita.	
INFORMACIÓN ADICIONAL	
FISQ: 5-163 SULFATO DE ALUMINIO	
ICSC: 1191	
© CCE, IPCS, 1994	
SULFATO DE ALUMINIO	
NOTA LEGAL IMPORTANTE:	Ni la CCE ni la IPCS ni sus representantes son responsables del posible uso de esta información. Esta ficha contiene la opinión colectiva del Comité Internacional de Expertos del IPCS y es independiente de requisitos legales. La versión española incluye el etiquetado asignado por la clasificación europea, actualizado a la vigésima adaptación de la Directiva 67/548/CEE traspuesta a la legislación española por el Real Decreto 363/85 (BOE 5.6.95).

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H6

Fichas Internacionales de Seguridad Química

HIDROXIDO DE ALUMINIO

ICSC: 0373

HIDROXIDO DE ALUMINIO Trihidróxido de aluminio $\text{Al}(\text{OH})_3$ Masa molecular: 78.0 Nº CAS 21645-51-2 Nº RTECS BD0840000 Nº ICSC 0373			
TIPOS DE PELIGRO/ EXPOSICION	PELIGROS/ SINTOMAS AGUDOS	PREVENCION	PRIMEROS AUXILIOS/ LUCHA CONTRA INCENDIOS
INCENDIO	No combustible. No inflamable.		En caso de incendio en el entorno: están permitidos todos los agentes extintores.
EXPLOSION			
EXPOSICION		¡EVITAR LA DISPERSION DE POLVOS!	
• INHALACION			
• PIEL			
• OJOS			Enjuagar con agua abundante durante varios minutos (quitar las lentes de contacto si puede hacerse con facilidad). después consultar a un médico.
• INGESTION			Enjuagar la boca, dar a beber agua abundante y someter a atención médica.
DERRAMAS Y FUGAS		ALMACENAMIENTO	ENVASADO Y ETIQUETADO
Barrer la sustancia derramada e introducirla en un recipiente, trasladarlo a continuación a un lugar seguro.		Separado de ácidos fuertes. Mantener en lugar seco.	Hermético.
VEASE AL DORSO INFORMACION IMPORTANTE			
ICSC: 0373 Preparada en el Contexto de Cooperación entre el IPCS y la Comisión de las Comunidades Europeas © CCE, IPCS, 1994			

Fichas Internacionales de Seguridad Química

HIDROXIDO DE ALUMINIO

ICSC: 0373

D	ESTADO FISICO; ASPECTO	VIAS DE EXPOSICION
A	Sólido blanco, en diversas formas (cristales monoclínicos, polvo, bolas o gránulos), inodoro.	La sustancia se puede absorber por inhalación.
T	PELIGROS FISICOS	RIESGO DE INHALACION
O		La evaporación a 20°C es despreciable; sin embargo se puede alcanzar rápidamente una concentración molesta de partículas en el aire.
S	PELIGROS QUIMICOS	EFFECTOS DE EXPOSICION DE CORTA DURACION
	En contacto prolongado con agua, forma geles ($\text{Al}2\text{O}3.\text{H}2\text{O}$); absorbe ácidos y dióxido de carbono.	
I	LIMITES DE EXPOSICION	EFFECTOS DE EXPOSICION PROLONGADA O REPETIDA
M	TLV no establecido.	La exposición crónica puede dar origen a un descenso del nivel de fosfato.
P	MAK: 6 mg/m³ (General limit for fine dusts) (1989).	
O		
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A		
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114

E S	
PROPIEDADES FÍSICAS	Punto de fusión: 300°C (véanse Notas) Densidad relativa (agua = 1): 2.42 Solubilidad en agua: ninguna Presión de vapor, kPa a °C: véanse Notas Presión de vapor, Pa a 20°C: <10
DATOS AMBIENTALES	
NOTAS	
Se indica el punto de fusión aparente originado por pérdida del agua de cristalización. Nombres comerciales: Alugel, Alumigel, Alusal, Amphogel, Almogastin, Higlife, Hychol 705, Hydrafil, Hydral 705, Liquegel, Martinal, Rehels F 1000.	
INFORMACION ADICIONAL	
FISO: 2-117 HIDRÓXIDO DE ALUMINIO	