60

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Señora Jefe de la
**DIVISION DE NUEVAS CREACIONES**
Superintendencia de Industria y Comercio
E. S. D.

**Tramite: 002**
**Evento: 001**
**Actuación: 538**

| | | |
|---|---|---|
| Referencia | : | Expediente No. **01.099.066** |
| Asunto | : | Solicitud de patente para: **ESPUMA DE POLIURETANO FLEXIBLE SOPLADA CON AGUA** |
| Solicitante | : | **ATOFINA CHEMICALS, INC.** |
| Fecha de Solicitud | : | 19 de Noviembre de 2001 |
| Publicada en | : | 27 de Junio de 2003 |

1. Yo, Emilio FERRERO, identificado como aparece al pie de mi firma, actuando como apoderado en el asunto de la referencia, atentamente, solicito se efectúe el examen de patentabilidad de la solicitud en referencia según lo establecido en el artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina. Para tal efecto presento junto con este escrito el recibo por valor de $335.000.00, que corresponde a la tasa fijada según lo dispuesto en la resolución No. 41687 del 24 de diciembre de 2002.

2. Ruego atentamente a la Señora Jefe se sirva ordenar que se anexe este recibo, para que se efectúe dicho examen y se continúe con el trámite de la solicitud.

Bogotá, - 5 DIC. 2003
Señora Jefe,

EMILIO FERRERO
T.P.A. No. 31.929

COLO 12362-801-001-9
MRE/PRP/ID-000104/WPC12362

61

SUPERINTENDENCIA Y COMERCIO

Radicacion : 01057066 00000001 Folios: 2

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NIT : 800176087 Tramite : 000 PRIMERIZA D 1 REGISTRO/ SIN PETICION

Dependencia: 2000 DIVISION DE NUEVAS ORGANIZACIONES

RECIBO OFICIAL DE CAJA : 03 - 85,511
FECHA : NOVIEMBRE 24 DE 2003

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

| DEPOSITANTE | TIPO PAGO | BANCO | CUENTA | No. PAGO | FECHA PGO | Vr. PAGO |
|---|---|---|---|---|---|---|
| CAVELIER ABOGADOS | CONSIGNACION | BANCO POPULAR | 050-00110-6 | 17923714 | 24/11/2003 | 28,427,560.00 |

***** C O N C E P T O *****

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

SON: TRESCIENTOS TREINTA Y CINCO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No._____

Odo 12362-801-001-9

Industria y Comercio
SUPERINTENDENCIA

**DIVISION DE NUEVAS CREACIONES**

RADICACIÓN EXPEDIENTE No. **01-99066**

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION** FUE PUBLICADO

EN LA GACETA DE PROPIEDAD INDUSTRIAL No **529**, DE FECHA **27** DE **JUNIO** DE **2003**, EL

TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL **24** DE **SEPTIEMBRE** DE **2003**.

**NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.**

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI ___ _____ NO ___ **X** _____

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

2020
Bogotá D.C., Noviembre 10 de 2005

Doctor
**EMILI FERRERO**
Apoderado **ATOFINA CHEMICALS, INC.**

| | | |
|---|---|---|
| **ASUNTO** | Radicación | 01-99066 |
| | Trámite | 002 |
| | Evento | 001 |
| | Actuación | 430 10822 |
| | Oficio | |
| | Folios | 012 |

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 tuvo en cuenta el capítulo descriptivo, comprendido en los folios 2 a 8 del expediente correspondiente a la solicitud en estudio, tal como fue radicado al inicio del trámite.

   B. El capítulo reivindicatorio tomado en cuenta para el presente estudio comprende 6 reivindicaciones y se encuentra en los folios 9 y 10, tal como fue radicado al inicio del trámite.

   C. Conforme lo establecen 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 19 de noviembre de 2001, en el momento de la radicación se reclamó prioridad. La copia certificada de la solicitud cuya prioridad fue reivindicada (US 09/717.806 de 2000-11-21) aparece junto con su traducción en los folios 20 a 42.

2. **Objeto de la invención:**

   A. Las reivindicaciones 1 a 6 de la solicitud en estudio se refieren a: un método para incrementar la blandura de la espuma de poliuretano flexible soplada con agua, dicho método comprende usar un agente de co-soplado que consiste de un hidrofluorocarbono seleccionado del grupo que consiste de 1,1,1,2- tetrafluoroetano, 1,1,1,3,3-pentafluoroetano, 1,1,1,3,3-pentafluorobutano y mezclas de los anteriores.

   B. El objeto de la solicitud se puede clasificar según la clasificación internacional como C 08 G 18/00.

3. **Claridad de la Solicitud:**

   A. El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina establece "la descripción deberá divulgar la invención de una manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

   En la descripción no se indicó el índice de dureza para el ejemplo comparativo.
   En el ejemplo 2 se empleó más cantidad de poliol que en el ejemplo 1. Luego, los resultados de estos dos ejemplos no serían comparables. En el ejemplo comparativo, la cantidad de poliol es menor que en los ejemplos 1 y 2. El resultado del ensayo de dureza tampoco sería comparable.

De acuerdo con lo anterior, la descripción no cumple con el requisito de claridad según lo establecido en el artículo 28 de la Decisión 486.

B. En el artículo 30 de la decisión 486 de la Comisión de la Comunidad Andina se establece: "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 que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple." En el artículo 51 se establece además: "El alcance de la protección conferida por la patente estará determinado por el tenor de las reivindicaciones."

i. Las reivindicaciones no se encuentran correctamente redactadas. Por su estructura todas las reivindicaciones deben constar de dos partes. Una primera parte, el preámbulo, sirve para situar el objeto de la invención dentro de un contexto técnico; es lo que se conoce y sobre lo cual no se reclama ningún privilegio. La segunda parte o parte característica, define lo que se considera novedoso y se desea proteger. Estas dos partes están separadas por expresiones como "caracterizado por" o similares. Debe corregirse el capítulo en especial las reivindicaciones independientes porque tal como están redactadas no está definida la materia que caracteriza la nueva creación que se pretende proteger.

ii. El solicitante caracteriza un producto por su uso en un método. Los usos y más específicamente los segundos usos no son características apropiadas para una invención según la legislación vigente. Sobre el particular esta Superintendencia ya hace varios años ha sentado su posición e incluso existe jurisprudencia andina al respecto, por lo cual sería conveniente que el solicitante quedara informado adecuadamente por parte de su apoderado.

iii. La palabra "formulación", en las reivindicaciones 5 y 6, no constituye un producto ni un proceso según lo establece el artículo 14 de la decisión 486 y por lo tanto no define la materia a proteger tal como lo exige el artículo 30 de la citada decisión andina.

iv. El capítulo reivindicatorio no debe contener frases o palabras ambiguas tales como "alrededor de" o "aproximadamente". Deben eliminarse.

De acuerdo con lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad según lo establecido en el artículo 30 de la Decisión 486. El solicitante deberá anexar un nuevo capítulo reivindicatorio con todas las correcciones aquí requeridas.

**4. Evaluación de la unidad de invención**

El artículo 25 de la decisión 486 de la Comisión de la Comunidad Andina establece: "La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo."

La presente solicitud carece de unidad de invención toda vez que configura tres objetos diferentes. Uno es un método para aumentar blandura en espumas poliuretánicas, otro es un método para producir espumas de poliuretano y un tercero es el agente de soplado. Los tres objetos de solicitud no comparten un concepto común inventivo porque los agentes de soplado ya eran conocidos en el estado de la técnica y se empleaban precisamente en la producción de espumas de poliuretano.

De acuerdo con lo anterior, la presente solicitud no cumple con el requisito de unidad de invención según el artículo 25 de la Decisión 486.

**5. Determinación del estado de la técnica:**

El artículo 16 de la Decisión 486 de la Comisión establece que: "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."

"Solo 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 esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40"

La fecha para determinar el estado de la técnica es el 2000-11-21, tomando en cuenta la prioridad reivindicada.

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 08 G 18/00, se encontró que antes del 2000-11-21 habían sido publicados los documentos enumerados en la siguiente tabla.

| No. | Documento | Título | Fecha de publicación |
|---|---|---|---|
| D1 | US 5,294,647 | Method for producing rigid foams and products produced therefrom | 1994-03-15 |
| D2 | US 5,688,834 | Catalysts which stabilize hydrohalocarbon blowing agent in polyurethane foam formulations | 1997-11-18 |
| D3 | US 5,409,962 | Substantially constant boiling blowing agent compositions of 1,1,1,2 – tetrafluoroethane and dimethyl ether | 1995-04-25 |
| D4 | US 5,395,859 | Catalysts which stabilize hydrohalocarbon blowing agent etc. | 1995-03-07 |
| D5 | US 4,996,242 | Polyurethane foams | 1991-02-26 |

**6. Evaluación de los requisitos de patentabilidad:**

El artículo 14 de la Decisión 486 de la Comunidad Andina establece que: "*Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial*".

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad del objeto de la solicitud reivindicado en la solicitud en estudio.

**A. Evaluación del nivel inventivo:**

El artículo 18 de la Decisión 486 de la Comisión de la Comunidad Andina dispone que: "Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

Todos los documentos citados en el numeral 5 del presente concepto mencionan los agentes de soplado (1,1,1,2- tetrafluoroetano, 1,1,1,3,3-pentafluoroetano, 1,1,1,3,3-pentafluorobutano)

que caracterizan el método reivindicado. Dichos fluorocarbonados ya eran conocidos desde antes de presentada la solicitud en estudio y tenían la misma finalidad que se le quiere dar en el método reivindicado: formar y abrir las celdas de la espuma. Cualquier técnico medio en la materia conoce el proceso de espumado de los poliuretanos en que se utilizaban clorometanos precisamente para dar suavidad a las espumas. El aumento de la suavidad o blandura debido al cambio por fluorocarbonados no se ha ilustrado en la solicitud y por lo tanto no se nota un efecto inesperado frente a los clorometanos.

Si bien los documentos encontrados en el estado de la técnica no siempre se refieren a espumas flexibles, un técnico medio en la materia conoce perfectamente que los agentes de soplado pueden ser utilizados también para la espuma flexible y la blandura no está dada únicamente por la cantidad de agente de soplado.

Por lo tanto, la solicitud en estudio no cumple con el requisito de nivel inventivo establecido por el artículo 18 de la Decisión 486.

**C. Resumen**

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

| No. | Documento | Reivindicaciones afectadas | Requisito afectado |
|---|---|---|---|
| D1 | US 5,294,647 | 1 a 6 | Nivel inventivo |
| D2 | US 5,688,834 | 1 a 6 | Nivel inventivo |
| D3 | US 5,409,962 | 1 a 6 | Nivel inventivo |
| D4 | US 5,395,859 | 1 a 6 | Nivel inventivo |
| D5 | US 4,996,242 | 1 A 6 | Nivel inventivo |

Se anexa copia de las anterioridades mencionadas.

**7. Notificación**

En cumplimiento del artículo 45 de la decisión 486 de la Comisión de la comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. 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 en el numeral 5.2, literal e) del capítulo quinto del título primero de la circular única No. 10 de 2001.

**ALIX CARMENZA CÉSPEDES DE VERGEL**
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 17 MAY. 2013.

| C NCEPTO TÉCNIC<br>Número: 1795 | EXAMINAD R TÉCNIC<br>Código: 202043 |
|---|---|

US005294647A

# United States Patent [19]

Blanpied et al.

[11] Patent Number: 5,294,647

[45] Date of Patent: * Mar. 15, 1994

[54] METHOD OF PRODUCING RIGID FOAMS AND PRODUCTS PRODUCED THEREFROM

[75] Inventors: Robert H. Blanpied; Robert J. Barlow; Andy L McLaughlin; Richard L. Donald, all of Meridian, Miss.

[73] Assignee: Atlas Roofing Corporation, Meridian, Miss.

[*] Notice: The portion of the term of this patent subsequent to Oct. 12, 2010 has been disclaimed.

[21] Appl. No.: 18,304

[22] Filed: Feb. 16, 1993

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 720,735, Jun. 25, 1991, and a continuation-in-part of Ser. No. 851,889, Mar. 16, 1992.

[51] Int. Cl.[5] ..... C08J 9/14

[52] U.S. Cl. ..... 521/129; 521/129; 521/130; 521/131; 521/170; 521/902

[58] Field of Search ..... 521/129, 130, 131, 125, 521/170, 902

[56] References Cited

U.S. PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| 3,993,609 | 11/1976 | Kamens et al. | 521/138 |
| 4,485,196 | 11/1984 | Speranza et al. | 521/172 |
| 4,572,865 | 2/1986 | Gluck et al. | 428/309.9 |
| 4,636,529 | 1/1987 | Crooker | 521/917 |
| 4,710,521 | 12/1987 | Soukup et al. | 521/118 |
| 4,714,717 | 12/1987 | Londrigan et al. | 521/131 |
| 4,898,893 | 2/1990 | Ashida | 521/131 |
| 4,927,863 | 5/1990 | Bartlett et al. | 521/131 |
| 4,960,804 | 10/1990 | Doerge | 521/130 |
| 4,981,879 | 1/1991 | Snider | 521/131 |
| 4,981,880 | 1/1991 | Lehman et al. | 521/902 |
| 5,032,623 | 7/1991 | Keske et al. | 521/131 |
| 5,091,436 | 2/1992 | Frisch et al. | 521/137 |

OTHER PUBLICATIONS

N. Malwitz, P. A. Mania, S.-W. Wong and K. C. Frisch, "Amine Catalysis of Polyurethane Foams"-Annual Polyurethane Conference-Oct. 15-17-1986-pp. 338-353.

*Primary Examiner*—Morton Foelak
*Attorney, Agent, or Firm*—Nixon & Vanderhye

[57] ABSTRACT

In a method of producing a thermosetting foam, a first of two foam forming blends ("A-Blend") is prepared using a multi-functional isocyanate such as polymeric polymethylene polyphenylisocyanate ("PMDI"). A second of two foam forming blends ("B-Blend") is prepared by mixing together a polyol; water; a tertiary amine catalyst having at least two hydrogen bonding sites for one molecule; and, an alkali metal organo-salt catalyst. The tertiary amine catalyst is of a type wherein both the hydrogen segment and the hydroxyl segment of water are attracted by both of the hydrogen bonding sites on the catalyst molecule essentially simultaneously. A first blowing agent is included with one of the two foam forming blends. When the first and second foam forming blends are mixed together, the tertiary amine catalyst quickly initiates a reaction predominately of the polymeric polymethylene polyphenylisocyanate with water (as opposed to a reaction with the polyol). The quick reaction of the PMDI with water causes, prior to a gel point of the foam, both (1) the production of a second blowing agent for forming cells in the blends and for causing expansion in the liquid blends; and (2) sufficient exothermic heat to initiate boiling of the first blowing agent. Relatively large amounts of alkali metal organo-salt catalyst induce rapid vaporizing of the first blowing agent due to a high level of exothermic heat, whereby expansion of the mixed blends is substantially completed prior to the effective conversion of the mixed liquid blends to a solid. According to the method, a degree of completion of expansion of the foam at any point in time exceeds a degree of completion of chemical reactions of the foam. In another mode of the invention, a frothing agent is also employed.

20 Claims, 5 Drawing Sheets

-continued

| Component | 9A | 9B | 9C | 9D | 9E |
|---|---|---|---|---|---|
| Total A-Blend: Reactivities | 252.58 | 252.41 | 257.21 | 252.41 | 253.57 |
| At Min Head: | | | | | |
| Temperature At Head: | 89° F. | 88° F. | 87° F. | 88° F. | 86° F. |
| Cream, Secs | 10" | 11" | 11" | 11" | 11" |
| Gel, Secs | 20" | 19" | 18" | 19" | 19" |
| String, Secs: | 26" | 28" | 25" | 25" | 27" |
| Tack Free Secs: | 34" | 40" | 34" | 37" | 40" |
| Free Rise Density: | 1.72 | 1.75 | 1.76 | 1.77 | 1.83 |
| Initial k: | 0.130 | 0.127 | 0.133 | 0.126 | 0.125 |

Foam Example No. 10

In Foam Example Number 10, KAT-25 is as described in B-Blend Example Number 3.

| COMPONENT | Pbw | Weight % |
|---|---|---|
| Stepan 2352 | 100.00 | 28.11 |
| DC-5098 | 2.50 | 0.70 |
| Polycat-5 | 0.25 | 0.07 |
| KAT-25 | 2.20 | 0.62 |
| Water Added | 0.84 | 0.24 |
| HCFC-141b | 21.03 | 5.91 |
| | 126.82 | 35.65 |
| PMDI | 217.52 | 61.13 |
| HCFC-141b | 10.92 | 3.07 |
| DC-5098 | 0.53 | 0.15 |
| | 228.97 | 64.35 |
| TOTAL FOAM | 355.79 | |
| Reactivities at 77° F. | | |
| Index: | 2.5 | |
| Cream, Seconds | 15" | |
| Gel, Seconds | 26" | |
| String, Seconds | 34" | |
| Tack Free, Seconds | 44" | |
| 100% Rise, Seconds | 94" | |
| Initial k, Hand Mix | 0.12 | |
| Density | 1.725 | |

While the invention has been particularly shown and described with reference to the preferred embodiments thereof, it will be understood by those skilled in the art that various alterations in form and detail may be made therein without departing from the spirit and scope of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of producing a rigid thermosetting foam, the method comprising the steps of:

(1) preparing a first of two foam forming blends using polymeric polymethylene polyphenylisocyanate;

(2) preparing a second of two foam forming blends by mixing together:

(a) a polyol;

(b) water in an amount less than 1% by weight of the total foam;

(c) a tertiary amine catalyst having at least two hydrogen bonding sites for one water molecule, wherein both the hydrogen segment and the hydroxyl segment of water are attracted by both of the hydrogen bonding sites on the catalyst molecule essentially simultaneously;

(d) an alkali metal organo-salt catalyst comprising a preblending of water, potassium hydroxide, and carboxylic acid;

(3) mixing a first blowing agent with one of the two foam forming blends;

(4) mixing together the first and second foam forming blends whereby the following occurs:

(a) the tertiary amine catalyst initiates a reaction between the water and the polymeric polymethylene polyphenylisocyanate whereby prior to a gel point of the

I) a second blowing agent is produced for forming closed cells in the blends and for causing expansion in the liquid blends;

ii) sufficient exothermic heat is produced to initiate boiling of the first blowing agent; followed by

(b) the alkali metal organo-salt catalyst induces rapid vaporizing of the first blowing agent due to a high level of exothermic heat, whereby expansion of the mixed blends is substantially completed prior to the effective conversion of the mixed liquid blends to a rigid solid, the alkali metal organo-salt catalyst being present in an amount sufficient to cause a sufficiently complete trimerization reaction.

2. The method of claim 1 wherein the carboxylic acid is acidic acid.

3. The method of claim 1, wherein the carboxylic acid is 2-ethyl-hexanoic acid.

4. The method of claim 1, further comprising mixing a frothing agent with at least one of the two foam forming blends.

5. The method of claim 4, wherein the frothing agent is chosen from a group consisting of $CHClF_2$, $CH_3CClF_2$, $CHClFCF_3$, $CH_2F_2$, $CHF_2CF_3$, $CH_3CF_3$, $CF_3CH_2F$, and $CH_3CHF_2$.

6. The method of claim 1, wherein the polymeric polymethylene polyphenylisocyanate has an average functionality greater than two.

7. The method of claim 1, wherein the tertiary amine catalyst is chosen from a group consisting of pentamethyldiethylenetriamine, bis(2-dimethylaminoethyl)ether, hexa-hydro-1,3,5tris(3-dimethylaminopropyl)triazine, and 2,4,6-tris(dimethylaminomethyl)phenol.

8. The method of claim 1, wherein the polyol is a polyester polyol having an average functionality between about 1.9 and 3.0.

9. A method of producing a rigid thermosetting foam, the method comprising the steps of:

(1) preparing an alkali metal organo-salt catalyst by preblending water, potassium hydroxide, and a carboxylic acid;

(2) preparing a first of two foam forming blends using polymeric polymethylene polyphenylisocyanate;

(3) preparing a second of two foam forming blends by mixing together:

(a) a polyol;

(b) water in an amount less than 1% by weight of the total foam;

(c) a tertiary amine catalyst having at least two hydrogen bonding sites for one water molecule, wherein both the hydrogen segment and the hydroxyl segment of water are attracted by both of the hydrogen bonding sites on the catalyst molecule essentially simultaneously;

(d) the alkali metal organo-salt catalyst of step (1);

(4) mixing a first blowing agent with one of the two foam forming blends;

(5) mixing together the first and second foam forming blends whereby the following occurs:

(a) the tertiary amine catalyst initiates a reaction between the water and the polymeric polymeth-

US005688834A

# United States Patent [19]

Parker et al.

[11] Patent Number: 5,688,834

[45] Date of Patent: Nov. 18, 1997

[54] **CATALYSTS WHICH STABILIZE HYDROHALOCARBON BLOWING AGENT IN POLYURETHANE FOAM FORMULATIONS**

[75] Inventors: **Robert Christian Parker**, Hamburg; **Timothy Rech Dennsin**, Grand Island, both of N.Y.

[73] Assignee: **AlliedSignal, Inc.**, Morristown, N.J.

[21] Appl. No.: **777,876**

[22] Filed: **Oct. 15, 1991**

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 752,396, Aug. 30, 1991, abandoned.

[51] Int. Cl.[6] ..... C08J 9/14; C08G 18/16; C08G 18/18; C08G 18/32

[52] U.S. Cl. ..... 521/118; 521/115; 521/124; 521/126; 521/127; 521/128; 521/129; 521/131; 521/163; 521/164; 521/166; 521/170; 252/182.2

[58] Field of Search ..... 521/118, 126, 521/127, 128, 129, 131, 163, 164, 166, 170, 124, 115; 252/182.2

[56] **References Cited**

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*Primary Examiner*—Rabon Sergent
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[57] **ABSTRACT**

The present invention relates to foam compositions which are expanded with hydrohalocarbon blowing agents in the presence of catalysts which result in a decreased amount of decomposition of the hydrohalocarbon blowing agents to haloalkenes during the polymerization. Thus, the present invention provides compositions comprising polyisocyanate, polyol, hydrohalocarbon blowing agent, surfactant, and at least one catalyst for polymerization of the polyisocyanate and polyol wherein the catalyst is less volatile than N,N-dimethylcyclohexylamine or the catalyst is a tertiary amine having at least one isocyanate-reactive functionality selected from the group consisting of —OH and —NH— and the catalyst results in a decreased amount of decomposition of the hydrohalocarbon blowing agents to haloalkenes during polymerization of the polyisocyanate and the polyol and especially during use of the foam samples at a temperature of at least about 54° C.

**9 Claims, No Drawings**

US005409962A

# United States Patent [19]

Bartlett et al.

[11] Patent Number: 5,409,962

[45] Date of Patent: * Apr. 25, 1995

[54] **SUBSTANTIALLY CONSTANT BOILING BLOWING AGENT COMPOSITIONS OF 1,1,1,2-TETRAFLUOROETHANE AND DIMETHYL ETHER**

[75] Inventors: Philip L. Bartlett; Joseph A. Creamer, both of Wilmington, Del.

[73] Assignee: E. I. Du Pont de Nemours and Company, Wilmington, Del.

[*] Notice: The portion of the term of this patent subsequent to Dec. 16, 2008 has been disclaimed.

[21] Appl. No.: 809,153

[22] Filed: Dec. 16, 1991

Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 723,112, Jun. 28, 1991, abandoned, which is a division of Ser. No. 492,963, Mar. 12, 1990, abandoned.

[51] Int. Cl.[6] ..... C08J 9/14; C09K 3/30

[52] U.S. Cl. ..... 521/88; 252/171; 252/305; 252/DIG. 9; 264/54; 264/DIG. 5; 424/45; 521/98; 521/114; 521/131; 521/146; 521/154; 521/155; 521/910

[58] Field of Search ..... 252/170, 171, 305, DIG. 9; 264/54, DIG. 5; 521/98, 131, 910, 88, 114, 146, 154, 155; 424/45

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*Primary Examiner*—Linda Skaling
*Attorney, Agent, or Firm*—Michael K. Boyer

[57] ABSTRACT

Substantially constant boiling blowing agent compositions of 1,1,1,2-tetrafluoroethane and dimethyl ether.

4 Claims, No Drawings

US005395859A

# United States Patent [19]

Demmin et al.

[11] Patent Number: 5,395,859

[45] Date of Patent: Mar. 7, 1995

[54] **CATALYSTS WHICH STABILIZE HYDROHALOCARBON BLOWING AGENT IN POLYISOCYANURATE FOAM FORMULATIONS DURING POLYMERIZATION**

[75] Inventors: Timothy R. Demmin, Grand Island; Robert C. Parker, Hamburg; Richard E. Elbeck, Orchard Park; Gary M. Knopeck, Lakeview; Donna M. Rezaaj, E. Amherst, all of N.Y.

[73] Assignee: AlliedSignal Inc., Morristown, N.J.

[21] Appl. No.: 752,295

[22] Filed: Aug. 30, 1991

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 718,528, Jun. 21, 1991, abandoned.

[51] Int. Cl.[6] ..... C08J 9/14; C08G 18/22; C08G 18/24; C08K 5/09

[52] U.S. Cl. ..... 521/125; 521/118; 521/123; 521/124; 521/126; 521/130; 521/131; 521/164; 521/170; 521/902; 252/182.24; 252/182.25; 252/182.26; 252/182.27; 252/182.28

[58] Field of Search ..... 521/118, 125, 126, 128, 521/129, 130, 131, 164, 170, 124, 123, 902; 252/182.24, 182.25, 182.27, 182.28, 182.26

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[57] **ABSTRACT**

The present invention relates to foam compositions which are expanded with hydrohalocarbon blowing agents in the presence of catalysts which are capable of decreasing the amount of decomposition of the hydrohalocarbon blowing agents to haloalkenes during the polymerization. Thus, the present invention provides compositions comprising polyisocyanate, polyol, hydrohalocarbon blowing agent, surfactant, and catalyst for polymerization of the polyisocyanate and polyol wherein the catalyst is capable of decreasing the amount of decomposition of the hydrohalocarbon blowing agents to haloalkenes during polymerization of the polyisocyanate and the polyol.

**26 Claims, No Drawings**

where $R_7$, $R_8$, and $R_9$ are the same or different and selected from hydrogen, bromine, chlorine, alkyl having 1 to 18 carbon atoms, and substituted alkyl and alkoxy having 2 to 18 carbon atoms containing —(O-)—$CH_2$—$CR_{10}R_{11}Cl$ where $R_{10}$ and $R_{11}$ are the same or different and selected from hydrogen, bromine, chlorine, aryl, and alkyl having 1 to 8 carbon atoms and a is 0 or 1.

The more preferred hydroxyalkylammonium carboxylates are of the formula $R_1R_2R_3N^+$—$CHR_4CR_5HOH$ $X^-$ and $R_1R_2R_3N^+$—$CH_2CR_4HOH$ $X^-$ where $R_1$, $R_2$, $R_3$, $R_4$, and $R_5$ are the same or different and selected from the group consisting of hydrogen and alkyl having 1 to 18 carbon atoms and $X^-$ is as defined above. An example of a more preferred hydroxyalkylammonium carboxylate includes DABCO® TMR-2® which is N-2-hydroxypropyltrimethylammonium formate, which is commercially available from Air Products and Chemicals, Inc. Other preferred hydroxyalkylammonium carboxylates include N-2-hydroxypropyldimethylethylammonium 2,2-dimethylpropanoate; N-2-hydroxyethyltrimethylammonium 2-ethylhexanoate; N-2-hydroxypropyl-trimethylammonium acetate; N-2-hydroxyethyltrimethylammonium 2,2,2-trichloroethoxyacetate; N-2-hydroxyethyltriethylammonium 2-chloroethoxyacetate; N-2-hydroxypropyltrimethylammonium trichloroacetate; and N-2-hydroxypropyltriethyl-ammonium 4,4,4-trichlorobutyrate.

Preferred N-substituted triazines are of the formula $C_3H_6N_3$—$[(R_{12}R_{13}C)_n NR_{14}R_{15}]_3$ where $n \cong 2$; $R_{12}$ and $R_{13}$ are the same or different and selected from hydrogen and alkyl having 1 to 18 carbon atoms; and $R_{14}$ and $R_{15}$ are the same or different and selected from alkyl having 1 to 18 carbon atoms, substituted alkyl having 1 to 18 carbon atoms, cycloalkyl having 1 to 18 carbon atoms, aryl having 1 to 18 carbon atoms, and substituted aryl having 1 to 18 carbon atoms. The more preferred substituted triazines include Polycat®41 which is hexahydro-1,3,5-tris[3(N,N-dimethylamino)propyl]-1,3,5-triazine which is commercially available from Air Products and Chemicals Inc. and hexahydro-1,3,5-tris[3(N,N-dimethylamino)ethyl]-1,3,5-triazine; hexahydro-1,3,5-tris[3(N,N-ethylmethylamino)propyl]-1,3,5-triazine; hexahydro-1,3,5-tris[3(N,N-diethylamino)-propyl]-1,3,5-triazine; and hexahydro-1,3,5-tris[3(N,N-dimethylamino)butyl]-1,3,5-triazine.

Preferred metal salts of chloroalkanoates are of the formula ($M^+X^-$) where $M^+$ is selected from the alkali metal ions $K^+$ or $Na^+$; or $M^{+2}(X^-)_2$ where $M^{+2}$ is selected from the alkaline earth metal ions $Ca^{+2}$, $Mg^{+2}$, or $Ba^{+2}$; and the dibutyltin divalent ion $(n\text{-}C_4H_9)_2Sn^{+2}$ where; and where $X^-$ is of the formula $R_{16}C(R_{17})(R_{18})CO_2^-$ wherein $R_{16}$ and $R_{17}$ are the same or different and selected from hydrogen, bromine, chlorine, and alkyl having 1 to 18 carbon atoms and $R_{18}$ is selected from chlorine, and substituted alkyl and alkoxy having 2 to 18 carbon atoms containing —$(O)_a$—$CH_2$—$CR_{19}R_{20}Cl$ wherein $R_{19}$ and $R_{20}$ are the same or different and selected from hydrogen, bromine, chlorine, aryl and alkyl having 1 to 8 carbons, and a is 0 or 1. Examples of the more preferred metal salts of chloroalkanoates include $K^+,{-}O_2CCH_2CCl_3$; $K^+,{-}O_2CCH_2OCH_2CCl_3$; $K^+,{-}O_2CC(CH_3CCl_3)H(CH_2)_3CH_3$; and $K^+,{-}O_2CC(OCH_2CCl_3)H(CH_2)_3CH_3$ wherein $K^+$ is selected from the cations listed above.

Preferred haloalkoxyacylated carboxylate salts are of the formula $M^+{-}O_2C$—$R_{21}$—$COO$—$CH_2$—$CH_2Y_b$ where $M^+$ is selected from alkali metal ions $K^+$ or $Na^+$ and from alkaline earth metal ions $Ca^{+2}$, $Mg^{+2}$, or $Ba^{+2}$; $R_{21}$ is selected from an alkylidene having —$(CH_2)_d$— where d is an integer from 1 to 3 or 1,2-phenylene, Y is bromine or chlorine, b is an integer from 1 to 3, and a+b=3. Examples of the more preferred haloalkoxyacylated carboxylate salts include $K^+,{-}O_2CCH_2COOCH_2CCl_3$; $K^+,{-}O_2C(CH_2)_2COOCH_2CCl_3$; and $K^+$, ortho —$(COOCH_2CCl_3)$ $C_6H_4COO^-$ wherein $K^+$ is selected from the cations listed above.

In accordance with this invention, any of these catalysts or combinations of these catalysts or their chemical equivalents may be used as described previously to prepare a variety of polyisocyanurate foams by standard techniques known to the art which may include the use of various standard additives such as surfactants, water, fire retardants, and others.

The typically used ratios of polyisocyanate to polyol and of blowing agent to these components may be used in practicing the present invention.

The use of these catalysts will provide rigid foams with significantly reduced levels of haloalkenes compared to the levels of haloalkenes found when using the catalysts commonly used in the rigid foam industry.

The amount of the catalysts employed in the present invention will vary depending upon the application, the type of foam being prepared, the identity of the polyol and other factors, but can readily be determined by anyone skilled in the art. The catalyst is used in an amount sufficient to polymerize the polyisocyanate and the polyol and also to decrease the amount of decomposition of the hydrohalocarbons to haloalkenes during the polymerization. Preferably, at least about 0.5 part catalyst per 100 parts by weight of polyol is used. More preferably, from about 0.5 part to 5.0 parts catalyst per 100 parts by weight of polyol are used.

Examples of polyols used in polyurethane modified polyisocyanurate foams include aromatic polyester polyols such as those based on complex mixtures of terephthalate-type or phthalate-type esters formed from polyols such as ethylene glycol, diethylene glycol, or propylene glycol. These polyols are used in rigid laminated boardstock, can be blended with other types of polyols such as sucrose based polyols, and used in other applications such as molded urethane foams.

Examples of polyisocyanates used in polyurethane modified polyisocyanurate foams include aromatic diisocyanates such as those based on mixtures of 2,4- and 2,6-toluene diisocyanate; these polyisocyanates are used in specialty foams. Another example is methylene diphenyl diisocyanate (MDI) which typically contains 5% diphenylmethane diisocyanates, 25% triisocyanates, and 20% higher polyisocyanates.

Any hydrofluorocarbon blowing agent may be used in the present invention. Preferred hydrofluorocarbon blowing agents include 1,1-difluoroethane; 1,2-difluoroethane; 1,1,1-trifluoroethane; 1,1,2-trifluoroethane; 1,1,1,2-tetrafluoroethane; 1,1,2,2-tetrafluoroethane; 1,1,1,2,2-pentafluoroethane; 1,1,1,3-tetrafluoropropane; 1,1,2,3,3-pentafluoropropane; and 1,1,1,3,3-pentafluoro-n-butane.

# United States Patent [19]

Lin

[11] Patent Number: 4,996,242

[45] Date of Patent: Feb. 26, 1991


[54] **POLYURETHANE FOAMS MANUFACTURED WITH MIXED GAS/LIQUID BLOWING AGENTS**


[75] Inventor: Chung Y. Lin, Orange, Conn.

[73] Assignee: The Dow Chemical Company, Midland, Mich.



[21] Appl. No.: 355,539

[22] Filed: May 22, 1989

[51] Int. Cl.[5] ..... C08K 5/00

[52] U.S. Cl. ..... 521/131; 252/67; 252/69; 252/182.24

[58] Field of Search ..... 521/131; 252/67, 69, 252/182.24



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[57] ABSTRACT

Disclosed are mixed halocarbon blowing agents comprising (1) halocarbons boiling below about 10° C., (2) halocarbons boiling between 20° C. and 35° C., and (3) inert organic liquids having a boiling point from about 35° C. to about 125° C.

Also disclosed are blends of the above mixed blowing agents with active hydrogen containing compounds, particularly polyols and the rigid closed cell foams prepared from such blends.

Up to 60 percent reduction in hard halocarbons is realized with the mixed blowing agents.


11 Claims, No Drawings

or the like. This serves to inhibit the rapid boiling off of the gas which helps to avoid the cooling/warming cycles usually encountered when dissolving gases in liquids. The temperature of the precooling is not critical but can fall within a range of from about 10° C. to about −20° C. The gas is passed into the solution until supersaturation is reached. This point is easily determined by trial and error methods but is most readily determined from material balance measurements, for example, difference in weight between the solution and the initial weight of the inert liquid. The saturated solution of (1) in (3) is allowed to return to ambient temperatures (about 18° to 24° C.) and the equilibrium concentration of the components determined using known analytical procedures, for example, vapor phase chromatography is an excellent method. Surprisingly, the solutions are stable for prolonged periods, for example, analysis after about one week at ambient temperatures shows no real decrease in component (1). The latter can be present in unexpectedly high proportions for a gas and it is not unusual to observe solutions wherein (1) is present in a weight percent range of from about 5 to about 20 percent in the inert liquid (3). However, when considering the overall component proportions of the blowing agents, it is desirable to express their values in respect of all three components which will be discussed below.

Once the gas has been dissolved in the inert liquid, the resulting solution can be routed in whatever direction is most convenient in leading to different aspects of the present invention. That is to say, it can be added as a separate stream along with all the other ingredients for making a foam. Alternatively, it can be premixed with the active hydrogen component and the intermediate halocarbon (2) prior to the foam formation step, or it can be premixed first with halocarbon (2). It is this latter route which leads to the mixed blowing agents of the invention and allows for a direct consideration of their respective proportions in the mixtures.

The gas/liquid solution is easily mixed with (2) using any mixing procedure desired under ambient conditions. No special precautions or cooling are required. The main objective of these blowing agent mixtures is the production of closed cell foamed polymers having maximum thermal insulation properties but with reduced levels of hard halocarbons. Accordingly, the proportions of the three components are governed by these considerations, by the foam densities desired, and, of course, by the maximum amount of the gaseous component which can be dissolved in the mixture. While almost any foam density within a range of from about 1.5 to about 20 pounds per cubic foot may be obtained, it is preferred to produce foams with densities in a range of from about 1.6 to about 4.0 p.c.f., most preferably, from about 1.8 to about 2.2 p.c.f. Additionally, those halocarbons falling within the group (2) are possessed of the optimum vapor pressures and K-factor properties for making foams with the most desirable properties. With all of these considerations in mind, the components are advantageously combined in the following weight percent proportions to total 100 percent: (1) from about 2 to about 25 percent, (2) from about 30 to about 90 percent, and (3) from about 8 to about 45 percent. Preferably, the proportions are from about 4 to about 10 percent, from about 50 to about 75 percent and from about 20 to about 40 percent, respectively.

The proviso that at least one of the components of the mixture contains at least one hydrogen atom is to ensure that at least one of the agents is a soft blowing agent thereby decreasing the level of hard component and thus decreasing the ozone depletion potentials. It is preferable that more than one hydrogen atom be present. However, there is a limit to the number of hydrogen atoms which can be present and still maintain optimum foam properties in any resulting closed cell foam polymer. The hydrogen containing blowing agent is not limited to any one particular component of the mixture. Additionally, each one of the components may contain hydrogens. However, to achieve maximum blowing properties with optimum hard blowing agent reduction, it is preferred that the gaseous component (1) and inert liquid (3) each contain hydrogen atoms.

Component (1) is described as a halocarbon defined above and as having a boiling point below about 10° C. making it gaseous under normal conditions of ambient temperature and atmospheric pressure. Generally speaking, the boiling point will fall within a range of from about 5° C. to about −50° C., preferably from about 5° C. to about −25° C., most preferably from about 5° C. to about −15° C. While this class of halocarbons can include aliphatic as well as cycloaliphatic compounds defined above with the appropriate halogen substitutions, the preferred subclass comprises haloalkanes having 1 to 2 carbons with a boiling point from about 5° C. to about −25° C. and preferably being substituted by chlorine and/or fluorine and hydrogen. Illustrative of component (1) are 1,1,2-trifluoroethane (F-143), 1,1-dichloro-1,2,2,2-tetrafluoroethane (F-114a), 1,2-dichloro-1,1,2,2-tetrafluoroethane (F-114), cyclic $C_4F_8$ (F-C318), 1-chloro-1,1-difluoroethane (F-142b), 1-chloro-1,1,2,2-tetrafluoroethane (F-124a), 1-chloro-1,2,2,2-tetrafluoroethane (F-124), bromodifluoromethane (F-22B1), 1,1,2,2-tetrafluoroethane (F-134), 1,1-difluoroethane (F-152a), 1,1,1,2-tetrafluoroethane (F-134a), dichlorodifluoromethane (F-12), 1-chloro-1,1,2,2,2-pentafluoroethane (F-115), perfluoropropane (F-218), chlorodifluoromethane (F-22), 1,1,1-trifluoroethane (F-143a), 1,1,1,2,2-pentafluoroethane (F-125), and the like, and mixtures thereof.

A preferred group of these halocarbons comprises 1,1-difluoroethane, 1,1,1-chlorodifluoroethane, 1-chloro-1,1,2,2-tetrafluoroethane, 1-chloro-1,2,2,2-tetrafluoroethane and mixtures thereof.

Component (2) is also defined above as a halocarbon but having a higher boiling point than (1). The boiling point falls within the range of from about 20° C. to about 35° C. It will be appreciated by one skilled in the art that this boiling range offers the optimum temperature for matching good blowing action with the vaporization of the halocarbon by the reaction exotherm of the polymer forming process. As in the case of (1) above, a preferred subclass comprises haloalkanes having 1 to 2 carbons and preferably substituted by chlorine and/or fluorine and hydrogen. More preferably, component (2) comprises a chlorofluoroalkane. Illustrative compounds are trichlorofluoromethane (F-11), 1,1-dichloro-2,2,2-trifluoroethane (F-123), and 1,1,1-dichlorofluoroethane (F-141b), and mixtures thereof.

Trichlorofluoromethane is particularly preferred.

Component (3) or inert organic liquid defined above can be regarded as the main solvent for the gaseous component (1). In this role it can have a relatively high boiling range because it is partially offset by the gaseous nature of (1). Accordingly, the boiling range can be from about 35° C. to about 125° C., preferably from about 40° C. to about 100° C. In its broadest scope, this solvent component can be selected from a much wider