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

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-011890- -00002-0000

Fecha: 2008-02-18 17:12:22 Dep. 2020 NUECREACIONE
Tia: 2 PATENTES Eve: 1 REGDEPOSITO
Act. 538 PETICION Folios: 2

Trámite : 011
Evento : 378
Actuación : 538

Referencia : Expediente No. 06011890
Asunto : SOLICITUD DE PATENTE PARA COMPUESTO ADHESIVO
QUE CONTIENE UNA MEZCLA A BASE DE ALMIDON DE
LEGUMINOSAS
Solicitante : ROQUETTE FRERES
Clase : C08L 001/000
Publicada en : La Gaceta No. 579 Del 31 de agosto de 2007
Fecha de Solicitud : 7 de febrero de 2006

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 presentada 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 \$420.000.00 correspondiente a la tasa fijada.

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.

Señora Jefe,

EMILIO FERRERO
T.P.A. No. 31.929

COLO-14742-801-001-0
MVNMGTVID-119226WPC14742
No. M-2008-119226\MVN

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 08 - 5,098
FECHA : ENERO 21 DE 2008

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-011890-00002-0000

Fecha: 2008-02-18 17:12:22 Dep. 2020 NUECREACION
Tra. 2 PATENTES Eve: 1 REGDEPOSITO
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***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO DE BOGOTA	062754387	2808479	21/01/2008	39,545,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	420,000.00
TOTAL :			\$ 420,000.00

SON: CUATROCIENTOS VEINTE MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

Colo 14742-801-0000

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 06-11890

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

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **579** DE

FECHA **31 DE AGOSTO DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA

LEY EXPIRA EL **28 DE NOVIEMBRE DE 2007**

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

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá, D. C., 6 de octubre de 2009

Doctor
Emilio Ferrero
Representante **Roquette Freres**

ASUNTO	Radicación	06-11890
	Trámite	002
	Evento	001
	Actuación	420
	Oficio	11850
	Folios	017

Patente de Invención	☒	Patente de Modelo de Utilidad	☐
Vía Nacional	☒		
Vía PCT (fase nacional)	☐	Cap. I	☐
		Cap. II	☐

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

1.1.	<u>Descripción:</u>	Folios: <u>38 a 60</u>	tal como se radicó inicialmente
1.2.	<u>Reivindicaciones:</u>	Folios <u>61 a 62</u>	tal como se radicó inicialmente
1.3.	<u>Prioridad:</u>	Folios: <u>63 a 80</u>	
		Fecha	7 de febrero de 2005
		País	Francia
		Número	0501215

2. Objeto de la invención

- Título de la solicitud (folio 1)
Compuesto adhesivo que contiene una mezcla a base de almidón de leguminosas
- Las reivindicaciones 1 a 12 de la solicitud en estudio se refieren a un **compuesto adhesivo para encolado de cartón ondulado que contiene partes primaria y secundaria, caracterizado porque la parte secundaria,**

constituida por almidones no gelatinizados y/o almidones hinchados, comprende esencialmente una mezcla de almidones de leguminosas y de almidones de cereales y/o de tubérculos, de modo que la proporción entre el almidón de leguminosas y almidón de cereales y/o de tubérculos esté comprendida entre 30/70 y 90/10, preferentemente comprendida entre 40/60 y 80/20 y, más preferente aún entre 45/55 y 75/25.

- El anterior producto busca mejorar los adhesivos para cartón.
- La Clasificación Internacional de Patentes (IPC) para esta solicitud es C08L1/00.

3. De la solicitud de Patente

Reivindicaciones (Artículo 30 D. 486)

El capítulo reivindicatorio de la solicitud en estudio presenta los siguientes defectos:

- *El solicitante caracteriza de forma incompleta la reivindicación independiente 1, toda vez que pretende que se le proteja un compuesto adhesivo que tiene dos partes, pero solo enseña la segunda parte. La reivindicación independiente debe ser clara y concisa, por lo que deberá señalar cuales son los componentes de la primera parte y de la segunda parte para poder establecer la comparación con el arte previo. Se sugiere combinar las reivindicaciones 1 y 2 formando la reivindicación independiente.*
- *La reivindicación 5 no es clara, en la medida que señala que uno de los componentes se encuentra entre un 10 y un 40% de la mezcla, pero no señala que compuesto es el que tiene dicha proporción. El solicitante deberá aclarar.*
- *La reivindicación 7 es ambigua toda vez que señala que la composición es libre de agua pero tiene "el agua de constitución de sus partes constitutivas" (sic). Luego no es claro si la composición tienen o no tiene agua. El solicitante deberá redactar de mejor forma dicha reivindicación y la idea que quiere expresar.*
- *Los componentes adicionales que figuran en la reivindicación 8 deberían estar dentro de la reivindicación principal. Debe recordarse que las reivindicaciones dependientes deben ser formas particulares de la reivindicación de la cual dependen, lo que conlleva a que dichos componentes deben estar definidos previamente. Como está redactado se entiende como una falsa dependencia.*
- *No son claras las proporciones que propone el solicitante; deberá establecer una base (peso total por ejemplo) y establecer todas las proporciones en relación a esa base.*
- *La expresión "esencialmente..." no permite delimitar el objeto de la solicitud, por lo que le solicitante deberá cambiarla.*
- *No se permiten expresiones como "en forma comercial seca", toda vez que, primero, es ambigua, y segundo, lo que se entiende en un país como comercial puede diferir notablemente como se entiende en otro país.*

Por lo anterior, el capítulo reivindicatorio no cumple con el requisito de definición, claridad, concisión o sustento por la descripción de acuerdo al art. 30 de la Decisión 486 y/o art. 22 Tratado PCT.

4. Unidad de invención (Artículo 25 D. 486)

La presente solicitud no tiene unidad de invención, dado que contempla diferentes conceptos inventivos relacionados así:

- *Composición adhesiva.*
- *Cartón ondulado*

Entre ellos no existe una relación dado que el cartón ondulado presenta características que no necesariamente tienen relación directa con la composición adhesiva de las primeras reivindicaciones. Se observa que el cartón es solo un uso que se le va dar a la composición adhesiva.

Por lo anterior, se puede concluir que la presente solicitud no cumple con el requisito de unidad de invención.

5. Reivindicaciones relativas a un uso o a un segundo uso (Artículos 14 y 21 D. 486)

La solicitud de patente, en lo referente a los usos, NO cumple con el artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones dado que:

- *Las reivindicaciones 10 a 12, especialmente la 12, buscan que se proteja el uso de la composición de las primeras reivindicaciones, algo que no se admite en la legislación colombiana.*

De lo anterior la(s) reivindicación(es) 10 a 12 no pueden ser consideradas invenciones patentables

6. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 7 de febrero de 2005
- Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación*
D1	WO 2004/044082	Aqueous adhesive composition based on legume starch	27.05.2004
D2	US 5 454 898	Fast setting starch based corrugating adhesive having partially hydrolyzed water soluble polyvinyl alcohol component	3.10.1995
D3	US 3 444 109	Paper laminating compositions comprising protein containing starch material	13.05.1969

7. Análisis de patentabilidad (Artículo 14 D. 486)

El solicitante pretende que se le proteja un compuesto adhesivo para encolado de cartón ondulado que contiene partes primaria y secundaria, caracterizado porque la parte secundaria, constituida por almidones no gelatinizados y/o almidones hinchados, comprende esencialmente una mezcla de almidones de leguminosas y de almidones de cereales y/o de tubérculos, de modo que la proporción entre el almidón de leguminosas y almidón de cereales y/o de tubérculos esté comprendida entre 30/70 y 90/10, preferentemente comprendida entre 40/60 y 80/20 y, más preferente aún entre 45/55 y 75/25.

El documento D1 relaciona un adhesivo dividido en dos partes, donde una parte comprende almidón de leguminosas, almidón de cereales, almidón de tubérculos o mezclas de ellos, donde una de las partes corresponde a almidones no gelatinizados.

Los documentos D2 y D3, cada uno de forma independiente, son un complemento del documento D1 y permiten que se encuentre en las combinaciones de documentos todo lo relacionado en el capítulo reivindicatorio de la presente solicitud.

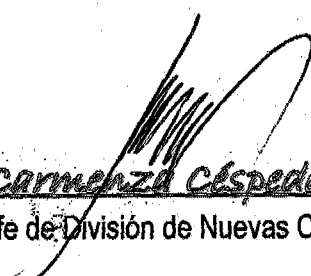
8. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	WO 2004/044082	1 - 12	Nivel inventivo
D2	US 5 454 898	1 - 12	Nivel inventivo
D3	US 3 444 109	1 - 12	Nivel inventivo

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 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 N° 10 de 2001.


Alix Carmenza Céspedes De Vergel
Jefe de División de Nuevas Creaciones

Concepto Técnico No. 3499
Examinador Técnico 202003

22 OCT. 2009

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

(19) Organisation Mondiale de la Propriété
Intellectuelle
Bureau international



(43) Date de la publication internationale
27 mai 2004 (27.05.2004)

PCT

(10) Numéro de publication internationale
WO 2004/044082 A1

(51) Classification internationale des brevets :
C09J 103/02

(21) Numéro de la demande internationale :
PCT/FR2003/003158

(22) Date de dépôt international :
24 octobre 2003 (24.10.2003)

(23) Langue de dépôt : français

(26) Langue de publication : français

(30) Données relatives à la priorité :
02/13910 6 novembre 2002 (06.11.2002) FR

(71) Déposant (pour tous les États désignés sauf US) :
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(75) Inventeurs/Déposants (pour US seulement) :
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(81) États désignés (national) : AE, AG, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ,
DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH,
GM, GR, GU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) États désignés (régional) : brevet ARIPO (GH, GM, KE,
LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), brevet
eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet
européen (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK,
TR), brevet OAPI (BF, BJ, CI, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Déclarations en vertu de la règle 4.17 :

— relative à la qualité d'inventeur (règle 4.17.iv) pour US
seulement
— relative à la qualité d'inventeur (règle 4.17.iv) pour US
seulement

Publiée :

— avec rapport de recherche internationale
— avant l'expiration du délai prévu pour la modification des
revendications, sera republiée si des modifications sont re-
çues

En ce qui concerne les codes à deux lettres et autres abrévia-
tions, se référer aux "Notes explicatives relatives aux codes et
abréviations" figurant au début de chaque numéro ordinaire de
la Gazette du PCT.

(54) Titre : AQUEOUS ADHESIVE COMPOSITION BASED ON LEGUME STARCH

(54) Titre : COMPOSITION ADHESIVE AQUEUSE A BASE D'AMIDON DE LÉGUMINEUSES.

(57) Abstract: The invention concerns an adhesive composition characterized in that it comprises an aqueous dispersion having a primary part, consisting essentially of a gelatinized starch, and a secondary part, comprising essentially a non-gelatinized starch and/or a swollen starch, wherein the starch of the secondary part is a native legume starch, and the starch of the primary part is optionally a native or modified legume starch, said legume starches having an amylose content ranging between 30 and 52 %. The invention also concerns the method for preparing such a composition, comprising its use, assembling the parts and drying and satisfying the requirements of modern fast machinery.

(57) Abrégé : L'invention a pour objet une composition adhésive caractérisée en ce qu'elle comprend une dispersion aqueuse présentant une partie primaire, constituée essentiellement d'un amidon gélatinisé, et une partie secondaire, comportant essentiellement un amidon non gélatinisé et / ou un amidon gonflé, dans laquelle l'amidon de la partie secondaire est un amidon de légumineuses natif, et l'amidon de la partie primaire est éventuellement un amidon de légumineuses natif ou modifié, lesdits amidons de légumineuses ayant une teneur en amylose comprise entre 30 et 52 %. L'invention a également pour objet le procédé de mise en oeuvre d'une telle composition, comprenant son application, l'assemblage des parties et le séchage et satisfaisant aux exigences des machines modernes et rapides.

REVENDEICATIONS

1. Composition adhésive caractérisée en ce qu'elle comprend une dispersion aqueuse présentant une partie primaire, constituée essentiellement d'un amidon gélatinisé, et une partie secondaire, comportant essentiellement un amidon non gélatinisé et / ou un amidon gonflé, dans laquelle:

- l'amidon de la partie primaire comprend un amidon choisi dans le groupe constitué par les amidons de légumineuses natifs et modifiés, les amidons de céréales natifs et modifiés, et les amidons de tubercules natifs et modifiés, seuls ou en mélange entre eux, et,

- lorsque l'amidon de la partie primaire comprend un amidon de légumineuses, l'amidon de la partie secondaire est alors choisi dans le groupe constitué par les amidons de légumineuses natifs, les amidons de céréales et de tubercules natifs et modifiés ayant une teneur en amylose inférieure à 30%, seuls ou en mélange entre eux, et,

- lorsque l'amidon de la partie primaire est un amidon de céréales ou de tubercules natif ou modifié, l'amidon de la partie secondaire comprend au moins un amidon de légumineuses natif,

lesdits amidons de légumineuses présentant par ailleurs une pureté supérieure à 90%, de préférence supérieure à 95%, et plus

préférentiellement encore supérieure à 98%, parallèlement à des teneurs inférieures à 1% (sec/sec) en matières colloïdales et / ou résidus fibreux, et inférieures à 1% (sec/sec) en protéines, et une teneur en amylose comprise entre 30 et 52% (sec/sec).

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2. Composition adhésive caractérisée en ce qu'elle comprend une dispersion aqueuse présentant une partie primaire, constituée essentiellement d'un amidon gélatinisé, et une partie secondaire, comportant essentiellement un amidon non gélatinisé et / ou un amidon gonflé, dans laquelle :

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- l'amidon de la partie secondaire est un amidon de légumineuses natif, et
- l'amidon de la partie primaire est éventuellement un amidon de légumineuses natif ou modifié,

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lesdits amidons présentant une pureté élevée, supérieure à 90%, de préférence supérieure à 95%, plus avantageusement encore supérieure à 98%, parallèlement à des teneurs faibles, par exemple et respectivement, inférieure à 1% (sec/sec) en matières colloïdales et en résidus fibreux, et inférieure à 1% en protéines, et une teneur en amylose comprise entre 30 et 52%.

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3. Composition adhésive selon la revendication 1 ou 2, caractérisée en ce que la teneur en amylose du ou des amidons de légumineuses est comprise entre 30,5 et 45%, de préférence supérieure à 31% et inférieure à 40%, notamment comprise entre 31,5 et 39,5% (sec/sec).

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4. Composition adhésive selon l'une quelconque des revendications 1 à 3, caractérisée en ce qu'elle comprend entre 10 et 40%, en poids, d'amidon de légumineuses, par rapport à la totalité de ladite composition.

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5. Composition adhésive selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle comprend 0,3 à 5%, en poids, d'une substance alcaline, par rapport à la totalité de ladite composition.

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6. Composition adhésive selon l'une quelconque des revendications 1 à 5, caractérisée en ce qu'elle contient 0,01 à 5%, en poids par rapport à l'amidon total, de borax ou de tout autre composé chimique porteur de bore.

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7. Composition adhésive selon l'une quelconque des revendications 1 à 6, caractérisée en ce qu'elle présente une matière sèche supérieure à 26% environ, de préférence égale ou supérieure à 28%.

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8. Composition adhésive selon l'une quelconque des revendications 1 à 7, caractérisée en ce qu'elle comprend une quantité efficace d'un agent chimique choisi parmi les sulfates, notamment, de zinc, d'alumine ou de cuivre, les composés porteurs de zirconium ou le phosphate de diammonium.

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9. Composition adhésive selon la revendication 8, caractérisée en ce qu'elle présente une matière sèche supérieure à 20% environ, de préférence égale ou supérieure à 22%.

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10. Composition adhésive selon la revendication 9, caractérisée en ce qu'elle présente une matière sèche supérieure à 24% environ, de préférence égale ou supérieure à 26%.

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11. Composition adhésive selon l'une quelconque des revendications 1 à 10, caractérisée en ce qu'elle comprend une quantité efficace d'une résine choisie dans le groupe constitué des résines formolées et des résines synthétiques non formolées.

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12. Procédé de préparation de carton ondulé, caractérisé en ce qu'il comprend, au moins une fois, les étapes suivantes:

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- application sur les sommets des cannelures d'une bande de papier préformée, d'une composition adhésive selon l'une quelconque des revendications 1 à 11,
- application d'un papier ou d'un carton plat sur les sommets de cannelures ainsi revêtus de la composition adhésive,
- séchage.

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13. Carton ondulé comprenant une composition adhésive selon les revendications 1 à 11.

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14. Carton ondulé selon la revendication 13, caractérisé par le fait qu'il présente une

résistance à l'eau selon les critères définis par le test FEFCO n°9.

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15. Carton ondulé selon l'une des revendications 13 ou 14, caractérisé en ce qu'il est choisi dans le groupe constitué par les cartons dits « simple face », « double face », « triple cannelure », les cartons dits lourds, les cartons présentant un nombre de cannelures supérieur à 3, et / ou des micro-cannelures.

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08005454898A

[54] FAST SETTING STARCH-BASED CORRUGATING ADHESIVE HAVING PARTIALLY HYDROLYZED WATER SOLUBLE POLYVINYL ALCOHOL COMPONENT

1731 Assignee: H. B. Fuller Licensing & Financing
Inc., Wilmington, Del.

[21] Appl. No.: 418,941
[22] Filed: Oct. 6, 1989

Related U.S. Application Data

[36] Continuation of Ser. No. 4,658, May 12, 1984, abandoned, which is a division of Ser. No. 330,669, Jan. 21, 1984, Pat. No. 4,673,698, which is a division of Ser. No. 751,462, Jul. 2, 1985, Pat. No. 4,604,735, which is a continuation of Ser. No. 612,339, May 21, 1984, abandoned.

[51] Int. Cl.⁶ C09J 4/00
 [52] U.S. Cl. 156/328; 106/213; 156/205; 156/210; 156/290; 520/67; 520/63; 520/57

[58] Field of Search 156328, 210,
1567205, 292, 52447, 53, 52, 106713

[56] References Cited

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2,116,937	127557	Basnet
2,142,548	631854	Elavasingh
2,155,555	291946	Kennedy
2,371,104	291946	Murphy et al.
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739 7/1985 Krankale
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45-19660	7/1/91U	Japan	156/322
49-122551	11/1/94	Japan	524/4
60-62475	3/1/95	Japan	
1514630	6/1/97	United Kingdom	

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24, pp. 156-173 Chapter entitled "waxes".

Primary Examiner—John I. Gallagher
Attorney, Agent, or Firm—Merchant, Gould, Smith, Edell,
Welber & Schmidt

ABSTRACT

Containing adhesives free of incompatibility problems with water soluble partially hydrotized polyvinyl alcohol compounds a major portion of water, starch, strong base, a boric acid compound and a partially hydrotized water soluble polyvinyl alcohol composition.

9 Claims, No Drawings

**FAST SETTING STARCH-BASED
CORROCATING ADHESIVE HAVING
PARTIALLY HYDROLIZED WATER
SOLUBLE POLYVINYL ALCOHOL
COMPONENT**

This is a continuation under 37 CFR 1.62 of prior application Ser. No. 079048-638, filed May 12, 1987, now abandoned, which is a division of U.S. application Ser. No. 066620-669, filed Jan. 21, 1986, now U.S. Pat. No. 4,673,106, which is a division of U.S. application Ser. No. 066751-699, which is a division of U.S. application Ser. No. 067151-462, filed Jul. 2, 1985, now U.S. Pat. No. 4,600,739, which is a continuation of U.S. application Ser. No. 066162-359, filed May 21, 1984, abandoned.

FIELD OF THE INVENTION

The invention relates to a starch based adhesive composition that can be used to form corrugated board. Moreover, particularly the invention relates to a starch based adhesive that rapidly increases in viscosity under conditions of heat and pressure resulting in a fast-setting green bond.

BACKGROUND OF THE INVENTION

[illegible]

The adhesives which have been developed to form these corrugated board or paper-based are generally starch based adhesives. The earliest corrugating board adhesive patent, U.S. Pat. No. 2,102,939, discloses an adhesive composition comprising gelatinized starch, ungelatinized starch, alkali and borax in a water base. This adhesive has formed the basis for the manufacture of essentially all corrugated paper-based to date. This adhesive is a cationic adhesive, whereas the balance of the starch forms an ungelatinized phase under conditions of heat and pressure the ungelatinized starch rapidly gelatinizes, absorbs water and causes a rapid increase in viscosity and adhesion of the starch-adhesive composition. Borax increases the level of viscosity as well as aiding final gelatinization.

More recently a number of patents have disclosed : corrugating board adhesives that can be characterized as conventional starch-based adhesive containing finely divided solid particles of a substantially room temperature

Insoluble/polyvinyl alcohol. The very insoluble polyvinyl alcohol disclosed in these patents became soluble at an elevated temperature. A substantially insoluble polyvinyl alcohol is used in these patents since the common belief of the conspiring industry is that soluble polyvinyl alcohol will gel in the presence of boxes containing starch based adhesives. The use of insoluble polyvinyl alcohol permits the use of the polyvinyl alcohol in starch based adhesives since at storage or ambient temperatures the polyvinyl alcohol, in solid form cannot interact with starch or other alcohols, in solid form cannot interact with starch or other alcohols, in solid form cannot interact with starch or other alcohols. After application to the glue tips, at conditions of high temperature and pressure, the polyvinyl alcohol can rapidly dissolve and substantially increase the viscosity and bond strength of the bond line between the corrugating medium and the liner material.

The need at which corrugating machines can be run is limited by the rapidity of viscosity increase in the bond line between the liner and corrugated medium. As the viscosity of the adhesive rises under conditions of heat and pressure in the corrugating process, a "green hour" is formed which holds the components together until the adhesive system forms the final heat-cured corrugated bond. The green bond relies solely on the viscosity of the product to maintain the integrity of the product during curing.

Conventional starch based adhesives rely on the rapid gelation of starch under conditions of heat and moisture to increase the viscosity of the adhesive during grain bond formation. More recent corrugating adhesives containing the additionally lamellar poly(vinyl alcohol) utilize the increase in viscosity that results as the poly(vinyl alcohol) is solidified at high temperature. However, both the conventional and the solid poly(vinyl alcohol) containing corrugating adhesives increase viscosity at a rate that leaves substantial room for improvement. If this rate at which viscosity increases occurs in the board line can be increased, then the corrugating machines can be run at a substantially increased temperature and the resulting increase in productivity increase in speed resulting in an increase in productivity.

Accordingly a substantial need exists for a corrugating adhesive having a faster set or a substantial increase in the rate of viscosity development or in the rate of green bond formation during the manufacture of corrugated board.

BRIEF DESCRIPTION OF THE INVENTION

We have learned the problems relating to the incompatibility of soluble polyvinyl alcohol compositions can be solved and an adhesive having a substantially improved heat set or increase in the rate of viscosity increase can be achieved by adding to a curable adhesive comprising starch, alkali base, borax and wet paper, a concentrated emulsion of a partially hydrolyzed soluble polyvinyl alcohol composition. We have found that, contrary to the teachings of this art, the incompatibility of polyvinyl alcohol compositions can be controlled by carefully controlling the amount of polyvinyl alcohol in relation to borax acid in the adhesive composition and by selecting a partially hydrolyzed polyvinyl alcohol composition. Further, a selection of a preferred lower molecular weight polyvinyl alcohol can improve the compatibility of the adhesive and the polyvinyl alcohol.

While we do not wish to be held to a theory of action of the intervention, we believe that the problems relating to phase-separation and gelling in poly(vinyl alcohol) containing aldehyde groups are directly related to an interaction between the hydroxyl groups of the starch or lactic acid and hydroxymethyl groups of the poly(vinyl) alcohol. We have found that these

harmful interaction ions can be prevented by controlling the available concentration of hydroxyl groups by controlling the concentration of polyvinyl alcohol in the solution and by selecting a partially hydrolyzed polyvinyl alcohol wherein a small but important proportion of the hydroxyl groups of the polyvinyl alcohol molecule remain acetylated. We have further found that in formulating corrugating adhesives with the partially hydrolyzed polyvinyl alcohol that there is a threshold concentration of the partially hydrolyzed soluble polyvinyl alcohol above which substantial gelling or incompatibility results. However, below the threshold polyvinyl alcohol acts to substantially increase fast set of the green bond or viscosity increase during corrugating board manufacture. Since the polyvinyl alcohol is in solution, the rate of green bond formation is increased by the presence of the alcohol, but is not limited by the rate of dissolution of a solid polyvinyl alcohol. Since green bond formation is increased corrugating machine speeds can be increased, proportionately. Still further we have found that the lower molecular weight polymers are more resistant to gel formation.

DETAILED DESCRIPTION OF THE INVENTION

Briefly, the novel water-resistant corrugated board adhesives of this invention are prepared by forming an aqueous emulsion having an alkaline pH containing a soluble partially hydrolyzed PVOH, starch, a strong alkali metal hydroxide base and a boric acid compound and optionally a basic resin crosslinking resin, and wax. The corrugated board adhesive of this invention is preferably formed from a suspension of starch particles in water. The viscosity and solids content are important factors influencing the speed with which the paper board machine can be operated and also affects the quality of the finished paper board. The suspending paste or carrier medium must be sufficiently viscous to maintain a smooth suspension of the starch particles, but not so viscous as to interfere with the application of the adhesive to the paper board. The nature and proportion of dissolved solids in the carrier medium influences both pot life and the speed with which a given paper stock absorbs water from the applied adhesive. The water content of the adhesive affects adhesive properties. A small degree of water absorption from the adhesive to the paper is desirable in forming strong bonds between the paper piles. Absorption of water beyond that required to give good bonding is undesirable since it robs the adhesive of water needed to complete the gelatinization of the suspended starch upon heating in the corrugator and leads to inferior bonding. The invention also relates to a dry blend composition, that can be diluted with water to form an adhesive. The dry blend composition comprises a major proportion of a starch composition useful in corrugating adhesives, and an effective amount of a cold water soluble partially hydrolyzed polyvinyl alcohol composition that can increase the rate of formation of a green bond during corrugated board manufacture.

Polyvinyl Alcohol

Polyvinyl alcohol (PVOH), a polyhydroxy polymer having a polyacetaldehyde backbone with pendant hydroxy groups, is a water soluble synthetic resin. It is produced by the hydrolysis of polyvinyl acetate. The theoretical monomer



does not exist. Polyvinyl alcohol is one of the very few high molecular weight commercial polymers that is water soluble. It is commonly available as a dry solid and is available in granular or powdered form. PVOH grades include a "super" hydrolyzed form (99.5% plus removal of the acetate group), a fully hydrolyzed form (99%+ removal of the acetate group), a form of intermediate hydrolysis (about 58 to 91% removal of acetate group), and a partially hydrolyzed (about 91% to 85% removal of the acetate group) polyvinyl alcohol. The properties of the resins vary according to the molecular weight of the parent polymer and the degree of hydrolysis. Polyvinyl alcohols are commonly produced in nominal number average molecular weights that range from about 20,000 to 100,000. Commonly the molecular weight of commercial polyvinyl alcohol grades is reflected in the viscosity of a 4 wt-% solution measured in centipoise (cP) at 20° C. with a Brookfield viscometer. The viscosity of a 4% solution can range from about 5 to about 65 cP. Variation in film flexibility, water sensitivity, ease of solution, viscosity, block resistance, adhesive strength, dispersing power can all be varied by adjusting molecular weight or degree of hydrolysis. Solutions of polyvinyl alcohol in water can be made with large quantities of lower alcoholic solvents and salt cosolvents. Polyvinyl alcohols can react with aldehydes to form acetals, and can be reacted with acrylonitrile to form crosslinking groups, and can be reacted with ethylene or propylene oxide to form hydroxy alkylene groups. Polyvinyl alcohols can be readily crosslinked and can be bonded to other gelatin.

Polyvinyl alcohol is made by first forming polyvinyl acetate or a vinyl acetate containing copolymers such as ethylene vinyl acetate copolymers and removing the acetate groups using a base catalyzed alkaline hydrolysis. The production of polyvinyl acetate or a vinyl acetate copolymer can be done by conventional processes which controls the ultimate molecular weight. Catalyst selection, temperatures, solvent selection and chain transfer agents can be used by persons skilled in the art to control molecular weight. The degree of hydrolysis is controlled by preventing the completion of the alkaline hydrolysis reaction. Polyvinyl alcohol is made in the United States by Air Products and Chemicals, Inc. under the trade name VINOLTM, by duPont under the trade name ELVANOLTM, and by Monsanto under the trade name CELVITOLTM.

The preferred polyvinyl alcohol compositions for use in this invention comprise polyvinyl alcohol made from a homopolymer or interpolymer of vinyl acetate that is partially hydrolyzed i.e. less than about 91% of the hydroxyl groups are free of acetate. The preferred partially hydrolyzed polyvinyl alcohol is available in low, medium or high molecular weight variations characterized by the Brookfield viscosity of a 4 wt-% aqueous solution at 20 degrees. The low molecular weight polyvinyl alcohol has a viscosity of about 4-10 cP, the medium molecular weight composition has a viscosity of about 15-30 cP and a high molecular weight composition has a viscosity of about 35-60 cP. The

preferred polyvinyl alcohol compositions have a reduced particle size adapting the composition for rapid dissolution. The particle size of the most preferred polyvinyl alcohol is such that 99+% of the product will pass through a -80 mesh screen.

The most preferred polyvinyl alcohol composition is made from a low molecular weight homopolymer of vinyl acetate that is partially hydrolyzed resulting in the removal of about 87% to 91% of the acetate groups from the vinyl acetate homopolymer.

Starch

The starch based adhesives of this invention are commonly characterized as being either a carrier adhesive, a no carrier adhesive, or a carboxylic carrier adhesive. The term carrier adhesive implies the presence of a thin base of gelatinized starch in which ungelatinized or nonhydrolyzed starch particles are emulsified or suspended. The term no carrier adhesive implies the substantial absence of gelatinized or hydrolyzed starch in the adhesive emulsion. The term carboxylic carrier adhesive implies that the distinction between gelatinized starch and ungelatinized starch is not clear in the adhesive composition. Generally carrier starch carrier adhesives are prepared in a way that a substantial amount of partly hydrated or partly gelatinized starch is formed. These terms are imprecise since during the preparation of the starch based adhesives some starch inherently becomes gelatinized during processing at any temperature. However substantial proportions of starch remain ungelatinized and nonhydrolyzed during preparation which can gelatinize and interact with PVOH, and borax during green bond formation.

The starch used in both the carrier phase and suspended starch phase is a commonly chemical product from a number of root, stem or fruit, plant sources. Starch is a high molecular weight polymeric carbohydrate polysaccharide, most commonly composed of six carbon monosaccharide units joined by alpha-glycosidic linkages having an approximate molecular formula of $(C_6H_{10}O_5)_n$, wherein n equals 10^5 to 10^6 . Starch occurs naturally in the form of white granules and comprises linear and branched polysaccharide polymers. Starch is commonly manufactured by first soaking and grinding the plant starch source, and separating the starch from waste matter. The starch is commonly reslurried and processed into a fluidized dried starch product. Commercial starch often has the form of a pear starch, powdered starch, light amylose starch, precooked or gelatinized starch, etc. Preferably pear starch is used in making both the carrier phase and the particulate starch suspended in the carrier.

Borax

The novel adhesive compositions of the invention contain a strong base which promotes the production of crosslinking species from the resin and acts to cure the adhesive. Borax is a strong base and can be used, however preferred bases are alkali metal hydroxides. The most preferred strong bases include sodium and potassium hydroxide. The strong base also lowers the gel point of the starch, which increases the rate of hydration of the starch during curing of the glue line.

Boric Acid Compound

The novel adhesive compositions of the invention include a boric acid compound which cooperates with the gelatinized and ungelatinized starch during heating and curing by reacting with available hydroxyl groups of the starch,

forming a starch borax complex which aids in gelling the carrier starch molecules and the suspended starch molecules. The cooperative reaction increases the tack of the adhesive and produces strong bonds. Any boric acid compound having free hydroxyl groups attached to the boron atom can be used, however commercial boric acid (orthoboric acid, H_3BO_3), and its hydrated form $H_3BO_3 \cdot xH_2O$ and borax (sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$) and other hydrate and anhydrous forms are commonly used. For a discussion of boric acid compounds such as boric oxides, boric acids and borates, see Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Vol. 3, pp. 608-652. The boric acid compound increases the tackiness, viscosity, and cohesive strength of the adhesive. As the adhesive cures in the glue line, a gel structure forms between the hydroxyl group of the polysaccharide, the boric acid compound and the PVOH. The exact mechanism of the crosslinking reaction between these compounds is unknown. Further, the heat buffers the caustic nature of the base used in the adhesive stabilizing the substrate to the hydrolytic effect of the base.

Crosslinking Resins

Resins that can be used in the novel adhesive compositions of this invention include resins that upon heating in basic media generate crosslinking species that react with and crosslink the hydroxyls in adjacent starch molecules. The crosslinking reagent tends to reduce the hydrophilic nature and the water solubility of the starch molecules by effectively removing the solubility of hydroxyl groups to water and by introducing aliphatic alkylene-type crosslinking moieties.

A preferred class of crosslinking resins comprise well known condensation products of the reaction of a ketone and an aldehyde compound. These resins are characterized as a polyether polymer but can contain a variety of other monomers such as urea, melamine, etc. In the presence of heat and bases, they commonly decompose to produce species that effectively crosslink the starch molecules. Preferred resins are acetone-formaldehyde resins, acetone-urea-formaldehyde resins, acetone-melamine-formaldehyde resins comprising 15 to 30 wt-% acetone, about 3 to 30 wt-% formaldehyde and 0 to 15 wt-% of third monomer. One example of the preferred crosslinking resin embodiment of this invention comprises the Kresak series of resins manufactured by American Cyanamide.

Wax

The term wax is used very broadly and is applied to a wide variety of materials. The materials can have properties resembling certain well known waxes or can be used to provide physical properties similar to those associated with well known properties of wax such as sealing, polishing, candle making, etc. Many waxy substances have been found in nature and have been known to be useful for many years. Historically waxes include substances that are natural products. Chemically, natural waxes are esters of fatty acids and monohydric fatty alcohols. Physically, waxes are water repellent solids having a useful degree of plastic character. However, modern waxes include various synthetic substances that can replace natural waxes in many preparations. The composition of natural waxes generally comprises an ester of a saturated fatty acid and a long chain monohydric alcohol. Long chain fatty acids often include acids having greater than 16 carbon atoms and most commonly about 26

carbon atoms. The aliphatic monohydric alcohol commonly has at least 14 and can range as high as 36 carbon atoms. Petroleum, mineral or other synthetic waxes often consist of saturated hydrocarbons having aliphatic or open chain structures with relatively low branching or side chains.

Particularly preferable waxes for the water resistant corrugated board adhesive are waxes such as petroleum waxes, candle wax, beeswax, etc. Particularly preferred waxes are the petroleum waxes such as microcrystalline waxes, slack waxes and paraffin waxes.

In somewhat greater detail, the novel fast set corrugating adhesives of this invention can be made by combining the ingredients in water and heating the mixture until a smooth uniform composition is formed. Preferably the adhesive is made by combining a starch slurry with a solution of the base in water heating the mixture to at least partially gelatinize the starch and then adding the remaining components under conditions of mixing to form the smooth corrugated adhesive. The adhesive can contain from about 5 to 75 parts of starch and about 0.1 to about 10 parts of base per 100 parts of the adhesive composition. In "carrier" adhesives the carrier phase comprises about 1 to 25 parts of starch and the ungelatinized phase comprises 5 to 30 parts of starch per each 100 parts of adhesive. The adhesive can contain about 0.1 to 5 parts of boric acid per each 100 parts of water and optionally about 0.1 to 5 parts of boric acid reacting crosslinking resin per 100 parts of water and about 0.1 to 5 parts of wax in an emulsion form per each 100 parts of water.

The fast setting adhesive of this invention contains about 0.01 to 2.0 parts of polyvinyl alcohol per each 100 parts of adhesive. Preferably the adhesive contains about 0.1 to 1.5 parts of polyvinyl alcohol and most preferably for reasons of rapid set and compatibility with the adhesive components about 0.25 to 1.25 parts of polyvinyl alcohol per 100 parts of adhesive. The ratio of polyvinyl alcohol to boric acid is important in the invention since the interaction between polyvinyl alcohol and boric acid can cause substantial gelling problems and the manufacture of the adhesive. Accordingly, polyvinyl alcohol is used in a ratio of less than 9 parts by weight of polyvinyl alcohol per each part of boric acid and most preferably 2 to 7 parts by weight of polyvinyl alcohol per each part of boric acid for reasons of obtaining a fast setting adhesive free of unacceptable component interactions. The invention also relates to a dry blend composition, that can be diluted with water to form an adhesive. The dry blend composition comprises a major proportion of a starch composition useful in corrugating adhesives, and an effective amount of a cold water soluble partially hydrolyzed polyvinyl alcohol composition that can increase the rate of formation of a green bond during corrugated board manufacture.

EXAMPLE I

Into a 12,000 milliliter stainless steel beaker equipped with an electrically driven blade mixer in a water bath heated to 140° F. was placed 3.336 kilograms of water. The water was permitted to reach a temperature of about 87° F. and 1.6 kilograms of pearl (corn) starch was added to the water. The contents of the beaker was mixed until uniform for 5 minutes and into the starch suspension was added slowly, drop-wise over a 10-minute period, a solution of 48 grams of sodium hydroxide in 834 grams of water. After the addition of the sodium hydroxide solution, the mixture was heated to about

94° F. resulting in a viscosity of 20 to 45 Zahn cup seconds. Into the blended, smooth emulsion of starch was added 20 grams of boric acid and 200 grams of water. The resulting starch based adhesive was 27.6 wt-% solids.

EXAMPLE II

Into 1,000 grams of the adhesive composition of Example I to a 1,200 milliliter stainless steel beaker equipped with an electrically driven blade mixer in a water bath heated to about 95° F. was added 12.0 grams of a 66 wt-% aqueous solution of an acetone-formaldehyde resin (0.2 mole % acetone), 4.0 grams of an aqueous 39 wt-% emulsion of slack wax, and 9.9 grams of a 15 wt-% aqueous solution of a low molecular weight (4-6 cp), partially hydrolyzed (87.0 to 89.0% hydrolysis) polyvinyl alcohol (VINOL 205—Air Products). The components were mixed until uniform.

EXAMPLE III

Example II was repeated except that the acetone formaldehyde resin and the slack wax emulsion were omitted.

TABLE I

Example	Rate of Bond Formation at 350° F.	
	No Bond after 4 seconds Bonded in less than 4 seconds	Bonded in less than 4 seconds
I		
II		
III		

In performing the above bond rate formal tests, the flutes of a single face liner (C-FILTR 69# W.S.S.20 W.S. MED, single face board) are coated with 12 mils of each adhesive. The glue lines on the flutes are connected with a liner sheet (69# W.S.S. liner sheet), and the assembly is placed liner sheet down on a hot plate at 350° F. A 3.92 kg. weight is placed on the assembly resulting in 34.95 grams per lined inch of glue line. The assembly is checked for bond formation.

EXAMPLE IV

Example was repeated except that the solvent of the partially hydrolyzed low molecular weight polyvinyl alcohol was replaced with a series of solutions having differing concentrations of a superhydrolyzed (99.3-9% hydrolyzed) medium molecular weight (22-26 cp) polyvinyl alcohol (VINOL 125—Air Products) as recorded in the following Table:

TABLE 2

Comparative Example	Solvent Polymer Concentration (wt %)	Adhesive Composition (wt %)	
		Amount Used (Grams)	Response
IV	15.0	0.5	Wet not set
V	7.5	0.5	Wet not set
VI	2.5	0.5	Wet not set
VII	2.5	1.0	Wet not set
VIII	2.5	1.5	Wet not set
IX	2.5	2.3	Wet not set
X	2.5	3.0	Wet not set
XI	2.5	4.0	Wet not set
XII	2.5	5.0	Wet not set
XIII	2.5	6.0	Wet not set

TABLE 2-continued

Comparative Example	Solvent Polymer Concentration (wt %)	Adhesive Composition (wt %)	
		Amount Used (Grams)	Response
5			

*The agitated adhesive and polymer solution immersed to fill the surface of small droplets of the polymer solution.
**The adhesive and polymer solution immersed to fill the surface of small droplets of the polymer solution.
***Polymer solution blended with adhesive but viscosity increase occurred.

Clearly a low concentration of the super hydrolyzed material causes substantial problems.

EXAMPLE XV

Into 1200 milliliter stainless steel beaker with an electrically driven blade mixer heated in a 140° F. water bath was placed 217 grams of water, 19.4 grams of pearl corn starch, and 1.6 grams of a low molecular weight (4-6 cp) partially hydrolyzed (87.0 to 89.0% hydrolysis) polyvinyl alcohol (VINOL 205—Air Products). The contents of the beaker were mixed until dissolution occurred at 125° F. After dissolution the mixture was agitated for 15 minutes and 200 grams of water were added. After the water addition the temperature of the mixture was less than 90° F. To the mixture was added drop-wise over a 10-minute period 110 grams of a solution of 6 grams sodium hydroxide and 104 grams of water. After the sodium hydroxide solution addition was completed the mixture was heated to 94° F. and the adhesive mixture had a viscosity of 12.85 Zahn cup seconds. Into the agitated mixture was added 2.5 grams of boric acid. The adhesive formed a strong green bond within 3 seconds at 350° F.

EXAMPLE XV

Into a 1200 milliliter stainless steel beaker equipped with an electrically driven blade mixer in a 140° water bath was placed 217 grams of water, 19.4 grams of pearl corn starch, and 2.4 grams of a low molecular weight (4-6 cp) partially hydrolyzed (87.0 to 89.0% hydrolysis) polyvinyl alcohol (VINOL 205—Air Products) having a reduced particle size. The mixture was heated to 108° F. for 25 minutes to solubilize the components. Into the mixture was added 200 grams of water which reduced the temperature to less than 88° F. Into the mixture was added drop-wise over a 10-minute period 110 grams of a solution of 6 grams of sodium hydroxide in 104 grams of water. After the addition the mixture was stirred until uniform and into the stirred mixture was added 2.5 grams of boric acid. The gel temperature of the adhesive was 138° F.

EXAMPLE XVI

Example XV was repeated except the polyvinyl alcohol was omitted and 200 grams of pearl corn starch was added in place of 197.6 grams of starch.

TABLE 3

Comparative Example	Rate of Bond Formation	
	Temperature °F.	Bond Time (Seconds)
3	350	3
4	300	6

TABLE 3-continued

Comparative Example	Rate of Bond Formation	
	Temperature °F.	Bond Time (Seconds)
5	250	10
6		14

Table 3 presents the bond of rate formal test of the adhesives prepared in Examples XV and XVI. Clearly the adhesive having the soluble partially hydrolyzed low molecular weight polyvinyl alcohol formed a significant bond at a much greater rate than the adhesive having no polyvinyl alcohol. Further, during the preparation of the Examples, the fine particle size of the polyvinyl alcohol solids permitted rapid solution.

The above discussion examples and data illustrate our current understanding of the invention. However, since many variations of the invention can be made without departing from the spirit and scope of the invention, the invention resides wholly in the claims hereinafter appended.

1 claim:

1. A method for the manufacture of corrugated board in which at least one liner is bonded to at least one fluted medium with an adhesive, which method comprises:

(a) obtaining a fluted medium;

(b) preparing an adhesive by contacting:

(1) a dry blend composition comprising:

(i) a major proportion of starch useful in corrugating adhesives; and

(ii) a cold water soluble, partially hydrolyzed polyvinyl alcohol, made from a homopolymer of vinyl acetate and having a degree of hydrolysis of less than about 91%;

(2) an alkali metal hydroxide;

(3) a boric acid component; and

(4) water to produce an aqueous emulsion comprising a major proportion of water, about 5 to 50 parts of starch per each 100 parts of adhesive, sufficient alkali metal hydroxide to provide an alkaline pH, about 0.1 to 5 parts of a boric acid component per each 100 parts of water, and an effective amount of the cold water soluble partially hydrolyzed polyvinyl alcohol sufficient to increase the rate of green bond formation wherein the concentration of the polyvinyl alcohol in the adhesive composition is about 0.5 to 1.5 parts of the polyvinyl alcohol per 100 parts of the adhesive composition;

(5) applying an effective bonding amount of the adhesive composition to the fluted medium to form a bond line;

(6) connecting the fluted medium with the liner at the bond line; and

(7) curing the bond line to bond the liner to the fluted medium.

2. The method of claim 1, wherein the weight ratio of polyvinyl alcohol to boric acid component is less than 9:1.

3. The method of claim 1, wherein the polyvinyl alcohol is a low molecular weight polyvinyl alcohol wherein the Brookfield viscosity of a 4 wt-% aqueous solution at 20° is about 4-10 cp.

4. The method of claim 1, wherein the partially hydrolyzed polyvinyl alcohol has a degree of hydrolysis of about 87 to 89%.

5. The method of claim 1, wherein the particle size of the polyvinyl alcohol is less than 80 mesh.

May 13, 1969

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PAPER LAMINATING ADHESIVE COMPOSITIONS COMPRISING
PROTEIN-CONTAINING STARCH MATERIAL
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PAPER LAMINATING ADHESIVE COMPOSITIONS
COMPRISING PROTEIN-CONTAINING STARCH
MATERIAL

Alexander J. Golick, Seattle, and John T. Shephard, Long-
view, Wash., assignors to Westco Corporation, Long-
view, Wash., a corporation of Washington.
Continuation-in-part of application Ser. No. 844,722,
Oct. 6, 1959. This application Feb. 11, 1966, Ser.
No. 576,238.

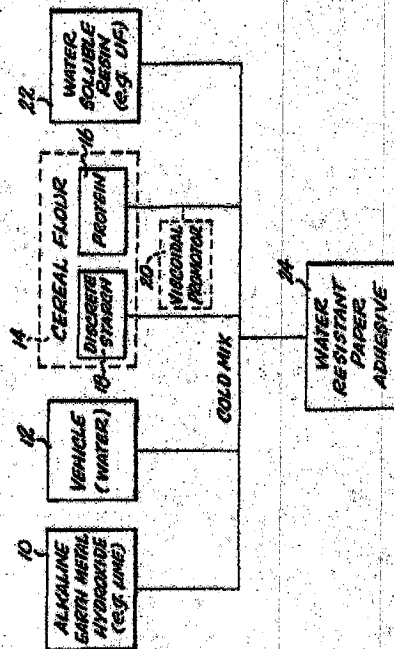
This portion of the term of the patent subsequent to
Aug. 15, 1964, has been disclaimed.

Int. Cl. C08g 57/38, 57/52; C09f 5/18

U.S. Cl. 260-4

ABSTRACT OF THE DISCLOSURE

Paper laminating adhesive compositions, certain of which are especially adapted for the bonding of corrugated board stock under commercial production conditions, with high-speed bonding and highly adhesive bonded product water resistance, such adhesive compositions being characterized by a first resistant in the form of a finely divided, substantially adhesive, potentially starch primary material having a protein content of at least about three percent by weight and an ungelatinized starch content of from about 15 percent to about eighty percent by weight, a second resistant which serves as a starch gelatinization agent and is a slightly water-soluble alkaline earth metal hydroxide forming material such as lime, providing by chemical reaction with the adhesive first, and a third resistant in the form of a starch resistant material selected from the group consisting of urea-formaldehyde liquid resins, ketone-aldehydes liquid resins, and other water-resistant materials. Additive components can also be employed, such as viscosity modifying agents, fungicide and organic filler materials, amide water propellants, wetting agents, and preservatives.



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isolated starch such as cornstarch, or tapioca starch is suspended in about five times its weight of water, then about 10% caustic soda (based on the dry weight of the starch) is added, and the mixture is heated to about 130° F. or higher up to 195° F. to cause gelatinization of the starch resulting in a viscous aqueous adhesive slurry. The slurry is then used as the carrier or vehicle for the starch or substituted starch. The vehicle thus prepared is cooled to about 100° F., then the dry starch is added in sufficient amount to give an adhesive slurry set with heat in the bonding machine, such as a paper carrying machine. The final composition of the adhesive is then prepared by separate mixing stages with application of heat in first or greater stage of preparation of the adhesive, and with the starch slurry containing sufficient moisture to give a pH of about 10.5 to about 12.0. The resulting adhesive bond, using the Buser formulation, also has advantageous characteristics in terms of narrow gelatinization temperature range, and of not being subject to breakdown in a dry mix because of the moisture in a liquid dispersion vehicle and because of an inherent tendency in a caustic containing dry mix for "poor" gelatinization to occur. Also importantly, the Buser gelatinization is about 105° F. and therefore requires constant temperature control, and drying storage must be thermostatically controlled to provide suitable flow properties. At these conditions, the tendency toward premature gelatinization in production equipment is aggravated. In the present adhesive system, the liquid adhesive temperature is considerably below that of the Buser system and thus provides a greater margin of safety under commercial use conditions. Also, and of extreme importance in many applications, is the fact that the Buser adhesive is a caustic substance either when hottest or dried by evaporation, a dried product bonded with the Buser adhesive being subject to complete delamination in about 5 minutes when immersed in water. Further, the Buser formulation is not compatible to economical addition of water-soluble impurities such as urea formaldehyde resins.

Obviously important advantages characteristic of the adhesive system are also found in the manner of use thereof. Keeping in mind that it is customary to maintain a conventional adhesive at an elevated temperature during use in order that its flow properties be suitable for handling on production equipment, it is important to note that the adhesive system of the present invention is desirable and handable on production equipment while at room temperature, i.e., in the so-called "cold" condition. Cold handling of the adhesive creates an operating condition where the temperature differential between the equipment and the adhesive is generally greater, with a corresponding reduction in the tendency of the adhesive to prematurely gelatinize. Further, the inherently greater viscosity and lower handling temperature of our adhesive while being handled makes possible a reduction in the average gelatinization temperature at which the equipment is operated without danger of premature adhesive gelatinization. As direct consequences of a lower average gelatinization temperature, the heating cost requirement on the equipment is reduced, its production speed potential is increased, and any tendency of the product to shrink or warp due to excessive drying in the final stages of the forming equipment is also reduced. Also, a characteristic of our adhesive system which is of fundamental importance to the art is the fact that the water resistant compound is formable even at room temperature. In direct contrast to certain previous water resistant modifications of the Buser adhesive system, where elevated temperatures, unsuitable for substantial times are necessary to develop water resistant properties. As a consequence of

This application is a continuation-in-part of my co-pending and now abandoned application Ser. No. 844,722, entitled, "Paper Laminating Adhesives, Materials and Processes Concerning Same, and Products Formed Thereby," and filed Oct. 6, 1959.

This invention relates to cold mixed, fast settable adhesives for bonding thin porous and/or fibrous materials, laminating paper products, or laminating paper to wood, metal, porous, or fibrous materials, especially where enhanced water resistance is desired. More particularly the present invention relates to adhesives as employed on high-speed bonding machines for the production of paper products, such as corrugated paper board, laminated fiberboard, paper covered vessels, and the like, the resultant bond being highly satisfactory from the point of view of laminated product water resistance and production speeds, the adhesive system characteristic of the invention, nonetheless being inexpensive, easy to prepare and easy to handle in use.

Historically, early paper corrugating adhesives commercially involved a sodium silicate or like inorganic aqueous solution, with the adhesive setting by accelerated evaporation loss of the solvent vehicle through application of heat. A first major change in this commercial practice came in about 1935, involving an adhesive used in processes such as that disclosed in Buser U.S. Patent No. 2,102,937 for example, wherein is disclosed a starch dispersed in a premixed alkaline carrier containing gelatinized starch. To prepare the Buser adhesive, an

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gradient to the point where the discrete starch can gelatinize sufficiently fast in the bonding process to permit satisfactory production speeds. It is generally recognized, however, that the presence of a substantial amount of one or more highly water soluble alkali salts is deleterious to the water resistance properties of the dried adhesive bond, since the dried highly water soluble alkali salts present in the dry adhesive film redissolve rapidly when exposed to water, thereby weakening the bond.

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viscous type flow on dispersing of the material in water solution being identifiable with the "viscoid" characteristics such terminology presents. Further, it is to be recognized that various official formulations of a protein-containing and a starch-containing material or materials is possible within the scope of the quoted terminology and is within the skill of those in the art.

agricultural residues, and the like can also aid in viscosity control and also in the control of the penetration properties and the bonding power of the adhesive. Additionally, emulsive water repellants such as wax emulsions, resin emulsions, polyvinyl acetate emulsions, wood resins and solvents thereof such as Vinsol, and mixtures of such emulsions can be incorporated in a given adhesive system with various beneficial effects in water resistance, flow characteristics, adhesion, flexibility of the bond, and adhesion to the substrate. Many other additives can also be incorporated as desired. Producers of adhesives should be aware of the fact that many of the additives mentioned herein are also preferably included in a number known resins as in the art.

of penetration, for example. Wetting agents can also be employed, as desired. Preservatives such as borax and the chlorinated phenols are also preferably included in a manner known per se in the art.

life, calcium oxide, strontium oxide, barium oxide, and mixtures thereof. Beryllium hydroxide and sodium hydroxide are not included because of toxicity and expense. Magnesium hydroxide, zinc hydroxide, cadmium hydroxide and metallic hydroxide are not included because each is either relatively water insoluble or has insufficient effectiveness on water resistivity of the adhesive system, for purposes of the present invention. Also of course excluded from the laminae are the alkali metal hydroxides such as caustic soda, which do not materially enhance the water resistivity of the adhesive composition. If desired, the alkaline earth metal hydroxides listed

ent of our adhesive can also be formed "in situ" by the double decomposition reaction of an alkali metal hydroxide and certain alkaline earth salts which have a higher water solubility than the corresponding alkaline earth metal hydroxide. Such formation of the alkaline earth metal hydroxide, resulting "in situ" is oftentimes of advantage from the point of view of pH stability because of the inherent nature of the solution.

As is well recognized, commercial grades of various alkaline earth metal hydroxide forming materials, such as contemplated by the present invention, often include more or less minute amounts of caustic or other alkaline hydroxide forming materials as impurities. The usual commercial grades of alkaline earth metal hydroxide forming materials have been found satisfactory for the purposes of the present invention, and the foregoing considerations with respect to this ingredient of the instant formulations are not to be construed as precluding the use of commercial grade forms of the alkaline earth metal hydroxide forming materials involved.

Certain alkali metal salts such as sodium tripolyphosphate, tripotassium-phosphate, sodium hexametaphosphate, and the like have a very beneficial effect on the flow and adhesive properties of the finished adhesive containing appropriate percentages of these salts.

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compounds has the beneficial effect of raising the gelatinization temperature of our adhesive mix. These compounds fall into two groups which are rather specific in their action and are not related particularly one to another. Short chemical compounds are sodium chloride and other alkali metal chlorides, bromides, and iodides; calcium chloride and other alkaline earth metal chlorides, bromides, and iodides; hydrogen peroxide and compounds releasing hydrogen peroxide in water solution, calcium peroxide, barium peroxide, strontium peroxide, sodium peroxide and other reactive peroxide, and other per-oxygen compounds such as urea peroxide which release nascent oxygen when in contact with a water-cereal flour mixture, water soluble cupric salts such as cuprous sulfate, stannous chloride, bromine, arsenic, cupric arsenite, stannous sulfide, and the like, as well as various organic acids such as acetic, citric, lactic acid, and the like.

The halides of the alkali metals and alkaline earth metals are most effectively used by dry mixing with the flour element or dissolving in the water prior to making the cereal flour and water slurry, they may be added at any stage in the making process with good effect. Where a salt is present in the mixture it is best to add it in the mixing water. A mixture A was prepared from 100 g. of low grade hard wheat flour with 100 g. of water (70° F.) and 5 g. of calcium hydroxide and was used to have a gelatinization temperature of 124° F. to 135° F.

The addition of 2 g. of sodium chloride to this mix A produced a mix B which had a gelatinization temperature of 128° F. to 134° F. The addition of 4 g. of sodium chloride to mix A gave a gelatinization temperature of 133° F. to 144° F. The addition of 8 g. of sodium chloride to mix A gave a gelatinization temperature of 137° F. to 149° F. Apparently there is not a sharp change in gelatinization temperature beyond the addition of 4 g. of sodium chloride to mix A. The addition of 1 g. of cupric sulfate to mix A raised the gelatinization temperature to 139° F. to 151° F. The addition of 1 g. of cupric sulfate to mix B raised the gelatinization temperature to 147° F. to 157° F. The effect of sodium chloride and cupric sulfate on the gelatinization temperature of the mixtures was determined by the addition of 2 g. of calcium chloride to mix A raised the gelatinization temperature of the mixture to 137° F. to 139° F. The addition of 3 g. of sodium chloride to mix A raised the gelatinization temperature to 134° F. to 136° F. It is interesting to note that the addition of the non-chemical phosphates also seemed to narrow the range over which the gelatinization took place. The addition of 3 g. of citric acid to mix A raised the gelatinization temperature to 139° F. to 149° F. and simultaneously narrowed the temperature range over which gelatinization occurred. The addition of 1 g. of 30% hydrogen peroxide to mix B gave mix C which had a gelatinization temperature of 143° F. to 158° F. The addition of 1 g. of cupric sulfate to mix C elevated the gelatinization temperature further to 152° F. to 164° F. The effects of all of these various reagents capable of releasing the gelatinization temperature in general are thus seen to be additive, i.e., cumulative. Further experiments have shown that the order of addition of these materials does not materially change the cumulative effect. Generally the addition of from about 1% to about 8% of the gelatinization temperature raising chemical compound based upon the dry weight of the flour is effective.

In obtaining the resin constituent of the formulation in the present invention, the term "soluble" amino-alcohols, liquid resin" is to be construed as including any liquid, water soluble urea-aldehyde resin and the amino-aldehyde resins, including amino-aldehyde resin reaction products in which minor portions of other materials reactive to aldehydes, such as ammonium, monochloramine, ethylenediamine, diethylenetriamine, triethylenetriamine, triethylamine, glycidylamine, and the like may be present either in chemically reacted or unreacted form. The term

"urea-aldehyde liquid resin" is to be construed as including but not limited to urea-formaldehyde liquid resin, methyl ethyl ketone formaldehyde liquid resin, and mixtures thereof. While reaction to the addition of the various operative reagents for purposes of the present invention, it is to be noted that gelatinization and reaction of these resins are generally exclusive, the latter types of resins being apparently incapable of themselves because of lack of the appropriate polyfunctional reactive character to form the irreversible colloid type of polymer-metal-protein-resin complex characteristic of the invention. While the exact chemical and physical phenomena involved have not been fully explored, it is hypothesized that the protein, the alkaline earth metal cation, and the resin on setting form a complex characterized by sharp increase in protein molecular size and an irreversible gel system, presumably because of at least partial cross-linkage condensation of the phenomena.

That the resin constituent does not form a reaction product by cross-linkage in the usual way is indicated because many of the operative resin constituents in the context of the present invention are of the type that will not form the usual type of condensation reaction product under the stable conditions presented by the adhesive system here involved.

It is further theorized that the ungelatinized starch ingredients function at least primarily as an adhesive binding medium, i.e., to regularly bind the water of solution by gelatinization of the starch during passage of the heated adhesive product through the forming machine. In this sense, the starch is also bound to the slightly water soluble alkaline earth metal hydroxide functions substantially as effectively as a caustic soda solution, in terms of reducing the gelatinization temperature of the starch content of the adhesive solution. That an interesting colloid is formed from the aqueous adhesive at the invention is shown by supplying the aqueous adhesive formulation of the present invention to form a bead between laminated paper, from permitting the bead to cool and then drying the bead to form a solid bead, which with varying degrees of water resistance and bond strength, depending upon the nature of the resin and hardener present in the adhesive, though the laminates were not subjected to any heating of the overall flour means entirely unimplicated. This is due to the fact that an increase in the resin content and the starch content is not completely essential to the development of water resistance.

From the foregoing more or less general considerations and from the following particular examples of practice of the invention, several specific and numerous advantages of the invention are noteworthy. One important practical advantage is that for some gluing operations all of the ingredients except the water of dispersion can be introduced in dry form for marketing purposes. Thus, for example, the cereal flour, an alkaline earth-metal hydroxide such as hydrated lime, and the resin can be mixed and sold as a dry mix. The formulation at the point of use of the adhesive does merely involves mixing same with water. This procedure is to be contrasted with the previous requirement of preparing a heated, gelatinized starch type carrier in order to get effective dispersion of the potentially adhesive material in sufficiently fluid form. Potentially adhesive materials are important because the starch gelatinizing power of the caustic is so great as to cause local or "spot" gelatinization of the ungelatinized starch as water is added to the dry mix, which in turn is due to localized concentrations of caustic. It of course being known in the art that if the caustic concentration is sufficiently high, gelatinization of the starch occurs even at room temperature.

A second important advantage of the adhesive formulation of the present invention is that such adhesive has a remarkably fast bonding speed, permitting high production rates, which advantage is in turn traceable to the

fact that substantially all of the contained starch in the adhesive is in ungelatinized form right up to the time of bond, and that the temperature necessary for its gelatinization is comparable to that obtainable in caustic carrier. A further advantage is that the absence of the water resistance of adhesive bonds in laminated paper products characterized of the invention, and the low cost of the ingredients making up the formulation and particularly the cereal flour or the like, as compared with the isolated structures now in common use as the primary ingredients for paper adhesive systems. Advantageous also are the development of satisfactory stability for fast setting, consistent with superior water resistance, and the realization of high solids content in the adhesive solution, consistent with a sufficiently low viscosity to render the adhesive solution readily handleable on product forming equipment.

One valuable function of the lime in our adhesive system, as compared with the alkali used hydroxide of other paper adhesive compositions, is that lime does not have the undesirable effect of solubilizing the sizing used in the beater sizing of the paper used as liner or corrugating medium.

Where an adhesive is to be used on a corrugating machine it is desirable that the flow characteristics of the adhesive be such that the adhesive jumps readily from a storage tank and readily circulates through the applicator glue pans. A rheologic viscosity or sabb body is not desirable in such an adhesive. Generally speaking the viscosity should be as low as possible to facilitate spreading but not so low as to be thrown off a rotating applicator roll. Once which is thrown off the applicator is not only well but builds up on the paneled applicator in a most unnecessary frequent shutdown for cleaning. Plastic flow as distinguished from viscous flow is always present to a degree, where solid particles are suspended in a liquid medium. In all of the compositions of the present invention solid starch particles are present suspended in a viscous proteinaceous carrier. Such systems always show plastic flow to a degree depending on the percentage of solid particles present. The higher the concentration of particles the more pronounced is the tendency toward plastic flow. The flow and shape of the particles as well as their electrical charge have an important bearing on the flow characteristics as is well known and already elucidated in standard rheologic texts.

When a cereal flour is mixed with water a dough is first formed. The plastic-viscous properties of the dough are evident to anyone who has ever kneaded bread or baked a cake. Some flours are smoothly viscous and string out when flowing off a spoon, while others are "short" and tend to fall off a spoon in chunks. Flours which are smoothly viscous tend to spread better from roll applicators. A typical flour miller's description of one type of wheat flour which gives a smooth viscous dispersion is what is known as a "winter wheat, second clear." This is a term which describes the kind of grain and the particular portion of the grinding operation in a conventional roller mill flour mill where the second clear wheat flour has been "run" or segregated from the total grain. Most flour for cooking and baking purposes is milled on multiple roller mills. The United States Food and Drug Administration has established six classes of wheat flour. They are (1) flour, (2) enriched flour, (3) self-sifting flour, (4) phosphated flour, (5) bromated flour, and (6) whole wheat flour. All of these, except (6) whole wheat flour, are white flours and are often called "patent" flours. Any of these can be made from soft wheat or hard wheat. The higher gluten content of the hard wheats endures more gas bubbles during the leavening process and makes a better rising bread. Flour from soft wheats is used chiefly for biscuits, cake, pastries, and baking flour. Wheat is made into flour by a process called milling. The endosperm or white inner part of the kernel is separated from the bran or outer layer of the wheat kernel and from the germ by multiple grindings on roller mills and sifts.

In milling, the wheat grain is first cleaned to remove all dirt, rubbish, weed seeds, chaff, straw, etc. The clean grain is then washed, during which the bran becomes separated or made less brittle. The grain is then passed through crushing rolls which crack the grain and loosen the bran and germ from the endosperm. The broken pieces are then separated from each other by sifting. The crushing and sifting are repeated until as much as possible of the bran and germ are separated from the flour. After the first grinding the crushed wheat is separated by sifting into "first break flour," middlings, and bran. Each succeeding grinding roll is set up to grind flour and flour. After each grinding the middlings are usually separated from the bits of bran contained therein by air separation methods. The purified middlings are then ground on a flour mill to form a white flour. About 70-75% of white flour, also called "straight flour," is recovered from 100% of wheat grain. Straight flour is further graded into four grades: (1) patent, (2) first clear, (3) second clear, and (4) low grade. Patent flour is the most expensive and makes the whitest bread. The first clear and second clear grades are used for dark colored breads and when mixed with rye flour make rye breads. Second clear and low grades are frequently used for industrial purposes such as in wallpaper paste or for the extension of wheat resin plywood adhesives. White or straight flour usually contains from about 5% to about 20% of protein (the protein content being taken as 6.25 times N, the nitrogen content, as determined by the Kjeldahl-Wittmann-Gunning method). The protein in wheat flour consists of a number of individual protein materials. Two of these, "gluten" and "gliadin," are collectively called "gluten" and constitute about 85% of the total protein in the flour. The gluten is the tough, sticky substance which holds the carbon dioxide bubbles made by the yeast during the bread making and causes the dough to rise. The gluten can be separated from the flour by making a dough from the flour and water and kneading gently under cold running water. The starch granules are washed away until only a creamy sticky mass of gluten is left. The term "gluten" is used for rye and other flours as well as for wheat flour. While rye flour is made in a conventional roller mill process similar to the manufacture of white or straight wheat flour. The baking product known as whole wheat flour or Graham flour consists of all of the bran, usually in coarse particles and is generally unsuitable for use in the adhesive of the present invention because of the poor spreading property encountered by the coarse bran particles. A flour made by hammer milling or impact milling of the whole grain of wheat, rye, barley, and the like to give a fine ground flour containing bran, endosperm, and germ, all of which will pass through a 100 mesh screen, is quite suitable for use in our adhesive. Such a flour has a natural advantage of containing fine ground bran which acts to aid in controlling penetration of the adhesive. In order to be used a whole ground flour must be ground to a sufficiently fine and uniform mesh size so that good spreading properties result when wet mixed. Flours having a mesh distribution between about 80 mesh and about 400 mesh are satisfactory, the preferred range of flour particle size being about 100 mesh to about 325 mesh. As the readily understood by those skilled in the art, appropriate particle mesh size can be obtained by sifting with a coarse cereal mesh and grinding the coarsest flour in wet state either with or without other ingredients of the adhesive system preliminary to use of the adhesive. In other words, the particle size of the cereal flour is related to the particle size of the coarse flour to the adhesive as used, regardless of whether the flour is preground to size in dry state or ground in wet state during formulation of the adhesive.

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In use, the behavior of an adhesive on the corrugator directly related to the viscosity characteristics of the adhesive resulting from elevation of its temperature. There is a pronounced difference in behavior of typical adhesives when attacking the corrugator and the adhesive used in the manufacture of the corrugator. The difference is the range of temperature over which changes in viscosity takes place. In the case of the Besser alkaline starch adhesive the change in viscosity occurs over a comparatively narrow temperature range of from about two to about three degrees Fahrenheit, whereas in a typical calcium hypochlorite adhesive the gelatinization induced change in viscosity takes place over a range of from about five to about 10 degrees Fahrenheit. This extended gelatinization range is probably due to the combination of starch and present in the present adhesive.

The gelatinization temperature of an alkaline adhesive containing suspended discrete starch is governed by the pH of the environment. At a given alkaline pH, for example, a pH 11.0, there is an important difference in the temperature at which gelatinization begins for the typical amorphous alkaline starch adhesive as contrasted with the alkaline earth hydroxide dispersed cereal flour of the present invention. Generally speaking at a given pH level the alkaline earth hydroxide dispersed cereal flour starts gelatinizing at about 10 to 15 Fahrenheit degrees lower than the Bauer composition.

It is desirable for maximum efficiency in using our adhesives on commercially available corrugations to adjust the gelatinization temperature of the adhesive by adjusting the concentration of alkaline surfactant hydroxide and consequently the pH of the adhesive system. For maximum production speeds it is desirable to operate at as low a gelatinization temperature as possible consistent with trouble free operation of the adhesive pumping and distribution system and the adhesive applicator. A sodium octadecylcarboxylate corrugator operating at steam temperatures in the range of 374° F. provides considerable rather than enough the adhesive may be continuously recirculated through the adhesive tank at which heats up the adhesive even

When its storage tank runs out, adhesive resin is carried off by the reservoir pans on the corrugated sheet, and is deposited in the troughs in the corrugations in order to be used when the heat pickup. An adhesive resin, usually about 100 to 150° F. above the temperature above which the heat pickup occurs, is used to melt down the adhesive resin in the troughs to fluidity and to set down the heat transfer which is necessary to start the curing and thereby increase production speeds. The heat pickup is maintained at a temperature of 100 to 150° F. above the storage temperature, can be artificially maintained at more than the temperature finally attained by the bulk of the adhesive as a result of the heat absorbed in the curing process, and is maintained by the heat transmitting through the corrugator circuit and the heat transfer from the bulk storage tank to its surroundings.

When an adhesive starts setting up prematurely on a corrugated corrugator, trouble develops initially at two places, the stripper fingers in contact with the adhesive and the reservoir pans and the ash pipe carrying the adhesive from the reservoir pans back to the main storage tank.

When an adhesive increases in viscosity due to premature setting, the thickened adhesive accumulates on the stripper fingers and the glue spread becomes erratic with poor bond in the corrugated sheet.

If the adhesive prematurely increases sufficiently in viscosity to interfere with the outflow of adhesive either from the reservoir or through the nozzle, it will result in inadequate wetting of the substrate. The rheological characteristics of the adhesive must be such as to permit its flow under the conditions of application. If the adhesive is too viscous, it may not be able to penetrate the pores of the substrate, resulting in poor adhesion. On the other hand, if the adhesive is too fluid, it may not be able to hold its shape after application, resulting in poor adhesion.

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ties on the forming equipment while at room temperatures, i.e., "cold," and (2) the range in temperature within which the viscosity increase with increase in temperature. With pregressive elevation in temperature, our adhesive develops increase of viscosity more slowly and more uniformly than the Bauer adhesive and consequently is more free from circulator and spreader troubles. It is thought it is fast setting in ultimate bond formation. Our adhesive is generally operative over the pH range of about 9.00 to about 12.5 as measured with standard glass electrode Beckman pH electrometer model 9B (making no correction for sodium ion), the preferred range for operating on a modern corrugator is between pH 11.1 to about pH 11.5 corresponding to a neutralization temperature of about 135° F. to about 140° F.

various cereal forms differ in the kind and quantity of protein present. As a consequence, they differ in their ability to combine with a given alkaline earth metal cation. At a given level of concentration of a given alkaline earth hydroxide the various cereal forms extend over different pH's and consequently different gelatinization temperatures. A suitable procedure therefore in studying a newly obtained cereal flour for use in our propagating alkaline is to determine the curve showing variation of pH with concentration of the alkaline in heat hydrolysis to be used and also the curve showing the variation in gelatinization temperature with concentration of the alkaline earth metal hydroxide. From these curves it is then possible to choose the proper concentration of the alkaline earth metal hydroxide to be used to give the desired gelatinization temperature for the propagator to be used. The succeeding batches of adhesive can then be quickly checked against the pH versus concentration curve for control purposes.

A well be apparent from various of the following properties, setting forth last data concerning various adhesives of the present invention, as compared with adhesions characteristic of the present invention, as compared with adhesions characteristic of the present invention, two or more adhesions of the adhesive system thereof, two or more adhesions of the adhesive system thereof, two or more adhesions of the adhesive system thereof.

The most important features of the adhesive system of the present invention are that (1) the formulation does not include a significant amount of sodium hydroxide or other alkali metal hydroxide, and (2) that no heating of the material or precalcination of the starch is necessary in preparation of the adhesive solution prior to utilization of the adhesive in insect baiting operations.

to be measured by pulling the following values: a number of consecutive tests at different temperatures; a number of adhesives in water (ammonium FPL), a test considering accompanied test procedures (TAMPI), a test considering water resistance can be described in terms of "fiber failure," usually given in area percentage composition. If a sample on being soaked in the water at 70° F. for 24 hours is entirely in the fiber of the paper when two laminations are pulled apart, then the adhesive bond can be described as having 100% fiber failures, i.e., as having maximum water resistance. If the failure is entirely in the adhesive bond, then the result can be described as 0% fiber failure, i.e., as having low or no water resistance. If the result can be described in a percentage of fiber failure, the failure is partly in the fiber and partly in the bond. The result can be described in a percentage of fiber failure, for example and as the case may be, 30% or 50%, depending upon the comparison of the area of fiber failure with the area of bond failure.

"pull" given in percentage comparison with respect to another test. The strength of the paper itself. An adhesive bond which is at least as strong as the wet paper is characterized as having a 100% bond strength.

A third test characteristic is found in the time of drying. It is necessary to obtain an adequate dry bond approaching the length of the paper. Time of set is an important consideration because existing laminated product forming equipment, such as that in widespread use in making corrugated paperboard, involves passages of the formed paper-

board through a heater on a double-facer machine, the time of transit of unheated paper through the heater being about 5-15 seconds on the average. Obviously, an adhesive which requires 10 seconds to set can be run through a forming machine only about half as fast as an adhesive which requires but 5 seconds to set.

By gelatinization temperature is meant the Fahrenheit temperature at which the major viscosity increase occurs when determined by the method of plotting the logarithm of the viscosity against the temperature of a 100 gram sample of the adhesive. The major viscosity increase of a 250 ml. glass beaker of adhesive confined in a 250 ml. glass beaker immersed in a hot water bath of variable temperature with constant hand stirring using a Mercury type thermometer and maintaining pot more than 10° F. differential between the temperature of the water bath and the rising temperature of the wet mixed adhesive undergoing test. Practically all of the adhesive tested gelatinize over a range in temperatures and in our examples this range is reported by two temperatures, the lower temperature being the temperature at which the major viscosity increase in viscosity starts and the higher temperature being the temperature at which the adhesive attains the viscosity of a viscous paste. For example, a gelatinization temperature of 212-215° F. indicates that the major viscosity increase begins at 212° F. and continues to increase until a paste viscosity is reached at 215° F.

EXAMPLE 1

An adhesive composition was prepared by mixing 50 grams of low grade hard wheat flour and containing approximately 13.5% protein, 11% moisture content, 0.5% calcium, and the residue being largely starch, with 0.25 gram of sodium sulfite dissolved in 50 grams of 70° F. water (with a pH of 7.12) was smooth and homogeneous, the sodium sulfite serving to render the wheat flour dispersible in the water solution, i.e., viscidated. To the general flour thus modified, 30 grams of water at 70° F. was added along with 5 grams of Lauric UP-111 (a 65% solids, aqueous syrup form of urea-formaldehyde resin), the mixture then being further mixed until smooth and homogeneous.

The resulting adhesive mixture had a pH of 8.35, a viscosity of 8 when measured with a MacMichael viscosimeter operating at 22 m.p.m. and using a No. 26 wire and a No. 26 bobbin immersed 3 cm. in the adhesive, this viscosity reading being equivalent to about 160 centipoises at 70° F. In such viscosity testing equipment, the bobbin consists of a brass cylinder 1 cm. in diameter and 5 cm. long with an appended disk 2 3/4" in diameter and 1/4" thick.

In most instances in this and the following experiments two types of test procedures were followed: (1) preparation and testing of so-called "single-facet" specimens, and (2) preparation and testing of so-called "double-back" specimens. A single-facet test specimen involves a flat, rectangular foil or flutu bonded to a flat sheet, and simulates the bond formed between the corrugated center ply and the bonding liner first applied to a corrugated machine ply. A single-facet test specimen is characterized by a comparatively small area of contact in the bond area and by formation under comparatively high pressure so that comparatively much of the adhesive coating is squeezed out of the comparatively bond area, with the result that, of the two test procedures used, this single-facet test procedure is the more stringent. A double-back test specimen involves the application under pressure of the second liner to a reformed

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pronounced in a single-face test specimen, oftentimes a much greater degree of improvement appears in the corresponding double-back test specimen, with the latter specimens demonstrating commercially satisfactory properties. In detail, the single-face testing procedures involved in the following examples proceeded as follows:

Corrugated medium stock 36 g (left paper) was compressed around a mandrel to provide a fold on one side of the glue line. The glue line was then torn back to a 10 mm wide strip of adhesive, then immediately pressed against a sheet of left paper (right paper) on a heated platen for 10 seconds, the glue line at about 15 mm from the edge of the paper being thermostatically maintained at about 75°C. Upon removal from the platen, the dry bond between the liner and the fused corrugated medium was satisfactory to hold the two together. The specimen was aged for a few days at 70°C and 50% relative humidity before being subjected to water resistance tests. The water resistance test consisted of soaking the specimen in 70°C water for 24 hours. At the end of the soaking time the glues of the test specimens were separated by hand and the percentage of their failures and approximate bond strength were noted as indicated previously, in the event of failure entirely within the glue bond, a rating of 0% fiber failure is assigned to the specimen. In the event the failure is solely in the paper, the rating of 100% fiber failure is given. A bond strength equivalent to the paper strength itself is indicated as 100%.

The single-face adhesive bond prepared and tested according to this Example I spontaneously floated apart when tested for water resistance and was therefore rated as 0% fiber failure and 0% bond strength.

In detail, double-back test specimens were prepared as follows. The two sheets of the adhesive were cut in this and the following examples by cutting $4'' \times 4''$ pieces of the adhesive. The adhesive was then applied to the adhesive of single faces conformed board and spreading adhesives on the tips of the corrugations by pressing this adhesive on a piece of glass. The adhesive was then immediately applied to the adhesive of the corrugations by pressing this adhesive on a piece of glass. The regular layer about $4'' \times 4''$ was immediately mounted against the adhesive, coated with the adhesive, and the back transferring through the applied layer just as in the conventional application of the double back on a corrugated board. A mild uniform pressure of about 1/4 psi was applied to insure contact between the laminations of the specimen and of the specimen on the hot plate. The specimens were then aged for 5 days at $70^\circ \pm 2^\circ \text{F}$. and 50% relative humidity. After aging the test specimens were immersed in water at 70°F . for 24 hours and then tested while wet.

Quantitatively, it is considered that any given adhesive composition under test, in order to be commercially acceptable in terms of its wet strength properties, should exhibit at least about 50% fiber failure and at least about 50% bond strength in both single-face specimens and double-back specimens.

The double-back test specimens prepared and tested as according to this Example 1 spontaneously floated apart just as was the case with the corresponding single-face test specimens when tested for water resistance in the same manner and were therefore also rated as 0% fiber failure and 0% bond strength.

These examples 1 is indicative of the fact that when no alums or equivalent ingredient is present with the modified resin, the resin is not cured. When an amino aldehyde resin is employed therewith, no water resistance in the resulting adhesive bond is developed in either the single-face bond or the double-back bond. A similar test was made, substituting an acetone formaldehyde resin, "Ketac," and showed similar results.

EXAMPLE II

An adhesive composition was made by mixing 50 grams of the wheat flour of Example I rendered viscous by adding thereto 0.25 gram sodium sulfite dissolved in 60 grams of 70° F. water, 1.5 grams hydrated lime suspended in 30 grams of water were added to the modified wheat

