



No. 05-091194-00002-0001

Fecha: 2007-05-28 16:27:24 Dep. 2020 NUECREACIONE
Tra. 2 PATENTES Eve: 223 ANUALIDADES
Act. 411 PRESENTACION Folios: 2**Señor****JEFE DE LA DIVISIÓN DE NUEVAS C**
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
E. S.D.

EXPEDIENTE No. 05.091.194

**ASUNTO: Solicitud de Patente de Invención denominada ESPUMA
FLORAL MEJORADA CON ADITIVOS Y
PROCEDIMIENTO PARA FABRICARLA.****Solicitante: FENOCOL LTDA.****TASAS EXAMEN DE PATENTABILIDAD**

MARIA VICTORIA HENAO HERNÁNDEZ, identificada con cédula de ciudadanía No. 29.808.404 de Sevilla, Valle, abogada en ejercicio con Tarjeta Profesional No. 22.057 del C.S.J., obrando como apoderada de la sociedad FENOCOL LTDA., por medio del presente memorial me permito anexar lo siguiente:

- 1) El recibo No. 49967923 del Banco Popular de Tasas Oficiales por valor de CUATROCIENTOS CUATRO MIL PESOS M/TE (\$404.000), para el examen de patentabilidad de la Patente de de la referencia.

Por lo anterior, solicito muy amablemente se ordene el examen de patentabilidad de la patente de la referencia y para lo cual se me puede notificar en la CALLE 23N N° 3-33 OFC. 602, TEL.092-6673418, 092-6679599, CALI - VALLE .-Email. henaohernandez@telesat.com.co.

Del señor Jefe,

MARIA VICTORIA HENAO**C.C.#29.808.404****T.P. 22.057 DEL C.S.J.**

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 07 - 42.606
FECHA : MAYO 28 DE 2007

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
WITHERS OASIS COLOMBIA	CONSIGNACION	BANCO POPULAR	050-00110-6	49967923	22/05/2007	404.000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		85 EXAMEN DE PATENTABILIDAD DE INVEN	404.000.00
		TOTAL :	\$ 404.000.00

SON: CUATROCIENTOS CUATRO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 05-91194

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

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **574** DE

FECHA **30 DE MARZO DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA LEY

EXPIRA EL **03 DE JULIO 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

27 28

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

2020

Bogotá, D. C., 6 de julio de 2009

Doctora

María Victoria Henao

Representante **FENOCOL Ltda.**

ASUNTO

Radicación **05 - 91194**
Trámite **002**
Evento **001**
Actuación **430**
Oficio **08449**
Folios **021**

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. Descripción: Folios: 9 a 13 tal como se radicó inicialmente
1.2. Reivindicaciones: Folios 6 a 8 tal como se radicó inicialmente
1.3. Dibujos: Folios 14 tal como se radicó inicialmente

2. Objeto de la invención

- Título de la solicitud (folio 1) **Espuma Floral mejorada con aditivos y procedimiento para fabricarla**
- Las reivindicaciones 1 a 12 de la solicitud en estudio se refieren a:
 - 1.- Una espuma floral de resina fenol formaldehído, caracterizada porque comprende al menos un bactericida, al menos una fragancia y al menos un alimento para flor cortada en su forma terminada
 - 7. - Un proceso de fabricación de bloques de espuma floral de resina fenol -formaldehído que contiene aditivos caracterizado porque comprende las etapas de:
 - Estabilizar la temperatura de una resina fenol-formaldehído a una temperatura entre 14 y 22°C en un recipiente plástico,

- Mezclar la resina fenol formaldehído con un tensoactivo o surfactante del tipo etoxilados por al menos entre 30 y 120 segundos
 - Adicionar uno o varios pigmentos del tipo ftalo y un solvente o agente expansivo, que es una mezcla de hidrocarburos del tipo hexano, hasta homogenización total por un tiempo aproximado de 30 a 120 segundos
 - Verter en un molde para obtener bloques la mezcla homogenizada y sellarlo herméticamente y después de 30 a 60 minutos, retirar un bloque madre
 - Cortar le bloque madre en unidades comerciales
 - Colocar en una banda transportadora las unidades comerciales y mediante boquillas, alimentadas con aire presurizado, aplicar por aspersión una mezcla compuesta de al menos una fragancia, al menos un bactericida y al menos un alimento para flor cortada, bajo condiciones de temperatura y presión ambiente, donde dicha mezcla está constituida por entre 4% y 9% de fragancia, en un porcentaje de la mezcla, el bactericida entre el 0,3% y el 0,56% y el alimento entre el 48 y el 75%
- El anterior producto y el procedimiento de fabricación buscan *espumas mejoradas para ser utilizadas como bases para la elaboración de arreglos florales*
 - La Clasificación Internacional de Patentes (IPC) para esta solicitud es A01G5/04.

3. De la solicitud de Patente

3.1. Descripción (Artículo 28 D. 486)

La descripción de la solicitud en estudio presenta los siguientes defectos:

- Los dibujos son totalmente etéreos y no apoyan la descripción. El solicitante debe recordar que, según Decisión 486 en su artículo 28, "...la descripción de la invención indicará el nombre de la invención e incluirla la siguiente información...d) una reseña sobre los dibujos, cuando los hubiera; e) una descripción de la mejor manera conocida por el solicitante para ejecutar o llevar a la práctica la invención, utilizando ejemplos y referencias a los dibujos, de ser éstos pertinentes..." (subrayado fuera de texto). El solicitante debe recordar que los dibujos se deben presentar según las normas del dibujo técnico.
- De acuerdo a la legislación, "...las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción..." (subrayado fuera de texto); algo que no sucede en la presente solicitud. El solicitante refiere como nuevo una serie de etapas de un procedimiento, pero en la descripción no se explica porque se consideran nuevas esas etapas en comparación con los procesos tradicionales; habla de variaciones de temperaturas, mezclas en ciertos intervalos de tiempo, mezclas de compuestos, cortes, etc. pero nunca se explica en la descripción el porque son nuevos estos pasos. De la misma forma, si el solicitante considera varias de esas etapas conocidas, las mismas deberían estar en el preámbulo de la reivindicación y no en la parte característica, pero también debería hacer explícito en la descripción que está empleando etapas de uso corriente en el arte y explicar en detalle en que tecnología se manejaban, porque las aplican y como se acomodan a la nueva tecnología propuesta por el solicitante.

- En congruencia con el punto anterior, el solicitante deber recordar que la Decisión 486 exige que "...Artículo 28.- La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla. La descripción de la invención indicará el nombre de la invención e incluirá la siguiente información:... b) la tecnología anterior conocida por el solicitante que fuese útil para la comprensión y el examen de la invención, y las referencias a los documentos y publicaciones anteriores relativas a dicha tecnología; c) una descripción de la invención en términos que permitan la comprensión del problema técnico y de la solución aportada por la invención, exponiendo las diferencias y eventuales ventajas con respecto a la tecnología anterior..." Nótese que el solicitante no cumple con los puntos c) y d) de dicho artículo en la medida que no sustenta el arte previo y las diferencias.
- El solicitante refiere una serie de intervalos en condiciones de proceso y proporciones de ingredientes, pero no explica las razones por las cuales emplea esos intervalos y no otros. Por consiguiente, la descripción no sustenta la solicitud.

Por lo anterior, la descripción no cumple con el requisito de claridad y/o divulgación completa que permita su comprensión y ejecución de acuerdo al art. 28 de la Decisión 486 y/o art. 22 del Tratado PCT

3.2. Reivindicaciones (Artículo 30 D. 486)

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

- *El solicitante refiere como nuevo una serie de etapas de un procedimiento, pero no diferencia las etapas conocidas de las nuevas. Si el solicitante considera varias de esas etapas conocidas, las mismas deberían estar en el preámbulo de la reivindicación y no en la parte característica, pero también debería hacer explícito en la descripción que está empleando etapas de uso corriente en el arte y explicar en detalle en que tecnología se manejaban, porque las aplican y como se acomodan a la nueva tecnología propuesta por el solicitante.*
- *La espuma relacionada en la reivindicación 1 no necesariamente coincide con la fabricada a partir del procedimiento de la reivindicación 7, en la medida que la espuma obtenida por el procedimiento reúne una serie de características específicas que no las incorpora la espuma de la primera reivindicación. Lo anterior llevaría a que exista una falta de unidad de invención en la solicitud que debería ser analizada; se sugiere que la reivindicación 1 se vuelva dependiente de la reivindicación 7.*
- *Muchas de las características técnicas relacionadas en las reivindicaciones no tienen sustento en la descripción como lo exige la legislación.*

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:

- Como ya se expresó, la espuma relacionada en la reivindicación 1 no necesariamente coincide con la fabricada a partir del procedimiento de la reivindicación 7, en la medida que la espuma obtenida por el procedimiento reúne una serie de características específicas que no las incorpora la espuma de la primera reivindicación. Lo anterior llevaría a que exista una falta de unidad de invención en la solicitud que debería ser analizada; se sugiere que la reivindicación 1 se vuelva dependiente de la reivindicación 7.

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

5. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 9 de septiembre 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	US 4225679	Floral foam product and method of producing the same which incorporates a flower preservative and a bactericide	30.09.1980
D2	US 4119757	Floral display blocks of urea formaldehyde foam	10.10.1978
D3	US 4769437	Process for the production of phenolic resins	06.09.1988
D4	US 3697457	Self wetting foam product and method of making same	10.10.1972

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

De acuerdo a la solicitud, se pretende protección sobre:

- Una espuma floral de resina fenol formaldehído, caracterizada porque comprende al menos un bactericida, al menos una fragancia y al menos un alimento para flor cortada en su forma terminada
- Un proceso de fabricación de bloques de espuma floral de resina fenol – formaldehído que contiene aditivos

El documento US 4225679 relaciona una espuma floral, que puede ser de fenol formaldehído o de urea formaldehído, que incorpora ingredientes tales como azúcares o bactericidas. Dicho documento relaciona como común en el arte previo el empleo de aditivos en espumas; lo que el considera como problema es que dichos aditivos se descomponen por las características propias de las espumas y por consiguiente propone diseñar una espuma que no permita la descomposición de cualquier aditivo que se le agregue.

El solicitante para Colombia coloca como problema que las flores que se encuentran en las espumas tienen poca vida, no tienen fragancia, tienen contaminación bacteriana entre otras cosas, se resume en que no se le pueden agregar aditivos. El mismo solicitante hace alusión a dicha anterioridad y afirma como diferencia que "...este documento no menciona la adición de otros aditivos de mejora diferentes al azúcar como nutriente para las flores...", sin embargo, el hecho que no los mencione no implica que un experto en la materia no los pueda adicionar; aún más, es bastante más difícil preservar el azúcar que otros compuestos. De la anterioridad se desprende que

si se pueden emplear ciertos aditivos, otros menos complejos en estabilidad pueden también emplearse.

Por consiguiente, el documento D1 revela una espuma en la que pueden emplearse una gran variedad de aditivos sin que se descompongan, en la medida que puede contener aditivos que se descomponen fácilmente y no lo hacen. Esto conlleva a que el problema propuesto por el solicitante ya ha sido resuelto con anterioridad. De lo anterior, la anterioridad D1 afecta la patentabilidad de la solicitud colombiana.

De la misma forma que la anterioridad D1, la anterioridad D2 (US 4119757) ya ha solucionado el problema y permite el uso de una amplia gama de aditivos en espumas.

Todos los documentos enseñan procedimientos de preparación de espumas y por consiguiente pueden afectar la patentabilidad de la actual solicitud.

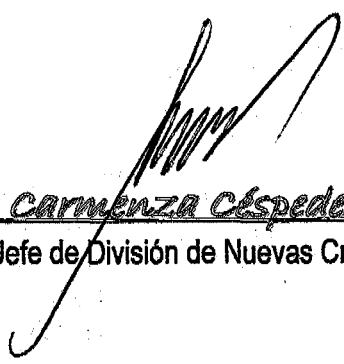
7. Conclusión:

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

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	US 4225679	1 - 12	Nivel Inventivo
D2	US 4119757	1 - 12	Nivel Inventivo
D3	US 4769437	1 - 12	Nivel Inventivo
D4	US 3697457	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. **2240**
 Examinador Técnico **202003**

23 JUL 2009

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

United States Patent [19]

Hobson et al.

[11]

4,119,757

[45]

Oct. 10, 1978

[54] FLORAL DISPLAY BLOCKS OF UREA-FORMALDEHYDE FOAM

[75] Inventors: John A. Hobson, Minneapolis; Paul
K. Schilling, St. Paul, both of Minn.

[73] Assignee: H & S Industries, Inc., St. Paul,
Minn.

[21] Appl. No.: 863,602

[22] Filed: Dec. 23, 1977

[51] Int. Cl.² B32B 3/26; B32B 5/18

[52] U.S. Cl. 428/311; 427/244;
427/430 R; 521/53; 521/109; 521/121;
521/188; 521/905

[58] Field of Search 428/311; 260/2.5 F;
427/244, 430 R

[56] References Cited

U.S. PATENT DOCUMENTS

2,753,277	7/1956	Smithers	260/2.5 F
2,900,278	8/1959	Powers et al.	427/244
3,197,327	7/1965	Dillon	427/244
3,826,674	7/1974	Schwarz	428/311

Primary Examiner—Morton Foelak

Attorney, Agent, or Firm—Orrin M. Haugen

[57] ABSTRACT

Hydrophilic floral display foam blocks are prepared from frothed urea-formaldehyde, and wherein the urea-formaldehyde contains an alkyl-aryl sulfonate, and wherein the alkyl-aryl sulfonate has been exposed to an aqueous solution of a quaternary ammonium salt in an amount sufficient to provide at least equal molar concentrations of the quaternary ammonium salt to the alkyl-aryl sulfonate present in the foam. The urea-formaldehyde foam may also contain quantities of sodium molybdate to enhance the stability and lifetime of cut flowers retained in the foam material. Also, the urea-formaldehyde foam may contain starch to help suppress the free formaldehyde odor and help increase the biodegradability of the cured foam. The resulting foam is hydrophilic in nature, and hence is readily wetted, with the hydrophilic characteristic not adversely affecting the life of cut flowers retained therein.

9 Claims, No Drawings

FLORAL DISPLAY BLOCKS OF UREA-FORMALDEHYDE FOAM

BACKGROUND OF THE INVENTION

The present invention relates generally to an improved floral display foam block, and more specifically to a floral foam display block prepared from frothed urea-formaldehyde resin. The urea-formaldehyde resin is treated so as to render the resultant foam hydrophilic in nature, and further providing for extended lifetime of cut flowers retained therein.

Urea-formaldehyde foam is a desired material for retention of floral displays, and has been widely utilized for such purposes in the past. Normally, however, urea-formaldehyde foam is hydrophobic upon curing, and may contain more than about 60% of closed cells in the foamed structure. The foam may be rendered substantially open cell by mechanically or physically crushing.

In the past, attempts have been made to render urea-formaldehyde foams hydrophilic through the soaking of a cured foam in an aqueous solution of a surfactant. However, it has been found that most surfactants, particularly those of the alkyl-aryl sulfonate type do not render the resultant cured foam product hydrophilic, inasmuch as the hydrophilic ends of the surfactant appear linked, bonded, or otherwise attached to the inside surfaces of the cured resin material. Furthermore, the use of alkyl-aryl sulfonates renders the moisture content of the foam generally anionic in nature.

It has been found that when the water content of a saturated floral display foam block is reasonably anionic, the water and the structure becomes toxic to cut flowers retained therewithin. While the reason for the toxicity is not precisely known, it appears to be due to the presence of toxic soluble salt levels, or toxic burning of the cut stems, thus generally prohibiting natural pathogens of the cut flowers to function efficiently or normally, and furthermore by not allowing the natural function of plant enzymes which regulate plant metabolism to function normally. Tests have verified that the quality of cut flowers deteriorates rather rapidly under these conditions. Evidence of the deterioration includes darkening of the stems, the drying of leaves, and the drooping of the flowers prematurely.

It has been found that the ionic balance of the foam may be adjusted by post-cure treatment of the foam with an equivalent cationic surfactant so as to control the ionic balance of the water. The alkyl-aryl sulfonate solutions are counter-balanced with an equivalent molar presence of quaternary ammonium salts, thus contributing to a double-decomposition of the alkyl-aryl sulfonates and quaternary ammonium salts through precipitation of an insoluble residual salt. As a result, the toxicity level of the foam is reduced, while the hydrophilic nature of the foam is preserved. The lifetime of cut flowers retained within the floral display foam increases, and exceeds that of the same cut flowers in water.

As a further feature of the invention, the pH of the foam is controlled to be at a desirable level, specifically in the range of approximately 3.5 to 4. Generally, urea-formaldehyde foams may have a pH of less than 2, which is normally the pH upon initial setting of the foam. Cured foam utilizing alkyl-aryl sulfonate stabilizers exhibit a pH of about 3.5 to 4.

SUMMARY OF THE INVENTION

Therefore, it is a primary object of the present invention to provide an improved hydrophilic floral display foam block of urea-formaldehyde foam wherein the foam block possesses qualities which preserve cut flowers for periods of time in excess of that available from water alone.

It is a further object of the present invention to provide an improved floral display foam block of urea-formaldehyde foam, and wherein the foam is rendered highly hydrophilic in nature, so as to expedite wetting of the foam without requiring forced emersion of the foam to achieve wetting.

It is yet a further object of the present invention to provide an improved hydrophilic floral display foam block of urea-formaldehyde, wherein the urea-formaldehyde foam contains a alkyl-aryl sulfonate surfactant together with a quaternary ammonium salt so as to achieve proper anionic balance of the foam for floral retention purposes.

It is yet a further object of the present invention to provide an improved floral display foam block of urea-formaldehyde foam which contains an alkyl-aryl sulfonate surfactant together with a quaternary ammonium salt to provide a desirable ionic balance, and further providing a substantially open cell configuration in the finished foam product.

Other and further objects of the present invention will become apparent to those skilled in the art upon a study of the following specification and appended claims.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In order to comprehend the preparation of the preferred embodiment of the present invention, the following examples are given.

EXAMPLE I

A commercially available urea-formaldehyde resin liquid is utilized, the liquid being mixed with 3.5% to 7% of sodium tertiary-butyl-benzene sulfonate by weight of solids of resin to sulfonate. A blowing agent is added to the resin-alkyl-aryl sulfonate mixture at the rate of 75 to 150 psi, the blowing agent being a continuous flow of compressed air within a closed chamber as is conventional in the art. The alkyl-aryl sulfonate mixture contains phosphoric acid in an amount of approximately 10% to 20% by weight of solids of resin to acid to catalyze the resin and expedite the setting thereof.

The set foam is then cut into blocks of the desired size, for example, 4 inches by 9 inches, and subjected to a mechanical crushing wherein a 3 inch cross-sectional thickness of the block is halved, and allowed to substantially recover to 3 inches.

The alkyl-aryl sulfonate stabilizes the foam, but provides a finished product which is generally hydrophobic. The block is thereafter immersed in a solution of a quaternary ammonium salt, specifically "Arquad S-50" available from Armour Industrial Chemical Co. of Chicago, Ill. The molar concentration of the quaternary ammonium salt in the aqueous solution is sufficient so as to be in molar excess to the alkyl-aryl sulfonate.

If desired, sodium molybdate is added in a quantity of approximately 0.01%, based upon the weight of the resin, with the sodium molybdate releasing molybdenum in a useful form for plants, with the molybdenum

3

assisting the plant in the fixation process of the root nodular microorganisms and in the nitrate reductase enzyme which controls reduction of inorganic nitrate into a form which the plant can utilize in building protein. Molybdenum has been designated as a key element in plant nitrogen metabolism, and also has other functions, such as being a requisite element for the synthesis of ascorbic acid and in the rendering of iron to be physiologically available within the plant. Molybdenum further alleviates plant injury caused by the presence of excessive amounts of other elements such as copper, boron, nickel, cobalt, manganese and zinc, all of which may be present in water solutions contacting cut flowers. The presence of the sulfate ion may decrease the amount of molybdenum which a plant may utilize, particularly from acid-based mediums.

EXAMPLE II

The urea-formaldehyde resin of Example I was treated with a blowing agent consisting of a continuous flow of compressed air, and wherein the blowing agent further contained approximately 3.5% by weight of the resin solids of an alkyl-aryl sulfonate, specifically sodium hexylbenzene sulfonate. To this formulation there was added 10% by weight of the resin solids of corn starch.

The material was heated to a temperature of 40° C. at which time frothing and setting were initiated, and the resin cured to a stable foam in a period of 8 hours.

Thereafter, the foam was cut into blocks of 4 inches by 9 inches in size, having a cross-sectional thickness of 3 inches and weighing approximately 35 grams. The cut blocks were then subjected to a compression operation in a press wherein the cross-sectional thickness was reduced to 1½ inches and thereafter the force was removed and the foam returned to approximately 3 inches. The block was then placed in a solution of a quaternary ammonium salt, specifically "Arquard S-50", wherein the quaternary ammonium salt was present in an amount of 3.9 grams per liter. The block was immersed and wetted to five times its weight of solution in the quaternary ammonium salt, after which it was permitted to dry at 21° C. In order to enhance the utilization of the floral display foam block, 0.04 grams per liter of sodium molybdate were added to the aqueous quaternary ammonium solution.

EXAMPLE III

The procedure of Example II was followed except that the alkyl-aryl sulfonate was sodium toluene sulfonate.

EXAMPLE IV

The procedure of Example III was followed with the exception that quaternary ammonium salt was utilized as the foaming agent, and alkyl-aryl sulfonate was utilized in the after-cure treating solution.

UREA-FORMALDEHYDE RESIN

Urea-formaldehyde resins are widely commercially available, and are normally prepared in a two-stage process in the presence of puridine, ammonia or alcohol. Heat is provided and the pH is controlled to form certain intermediates such as methylolurea or dimethylolurea which are mixed with certain stabilizers to produce liquid water condensate resins. The resins are later converted to a thermal setting resin by controlling

4

heating in the presence of a catalyst, such as, for example, in this instance, phosphoric acid.

ALKYL-ARYL SULFONATES

As has been indicated, alkyl-aryl sulfonates selected from the group consisting of sodium tertiary-butylbenzene-sulfonate, sodium hexylbenzene sulfonate, and sodium toluene sulfonate may be utilized. Other sodium sulfonates may be employed, along with certain potassium analogues, such as the potassium analogues to the three sodium sulfonates specifically listed hereinabove. As has been indicated, the utilization of sodium sulfonate provides a foam which does not become properly hydrophilic until exposure to quaternary ammonium salts, or vice versa, whereby the quaternary ammonium salts are the foam stabilizers and the alkyl-aryl sulfonates are the after treating solutions.

QUATERNARY AMMONIUM SALTS

While any of a variety of quaternary ammonium salts may be employed in aqueous solution, the following are preferred: Alkyltrimethylammonium chloride which is water soluble; Dialkyldimethylammonium chloride which is water insoluble; "Arquard S-50" being the alkyltrimethylammonium chloride, the alkyl portion of the compound having a chain length of from 8 to 18 carbon atoms, and specifically, in the above examples, 16 carbon atoms. Specifically, the alkyl portion may be the hexadecyl, the octadecyl, the octadecadienyl, or the octadecenyl radicals. Such materials are commercially available.

As has been indicated, it is the function of the quaternary ammonium salt to modify the exposed portion of the alkyl-aryl sulfonate so as to render the entire product hydrophilic in nature.

THE USE OF STARCH

The use of starch has been found to be desirable from the standpoint of reducing or in some cases, eliminating the odor of formaldehyde from the finished product. It is believed that the presence of starch, specifically corn starch, provides a reactive site for formaldehyde which may be released in the product both during preparation, and subsequently during use and exposure to water. Also, the starch helps the biodegradability of the foam.

USE OF FILLERS

Normally, the finished product will have a density of approximately 1.2 pounds per cubic foot, however this density can be increased by the addition of either more resin or iron filings, sand, diatomaceous earth or the like. Normally, a density of approximately 1.2 pounds per cubic foot is desired.

BACTERIOSTAT

If desired, a hydroquinone bacteriostat such as is commercially available may be added in an aqueous solution containing approximately 0.05% by weight of hydroquinone bacteriostat. The utilization of bacteriostat do assist in controlling bacteria growth.

UREA-FORMALDEHYDE RESINS CONTAINING ALKYL-ARYL SULFONATES

Urea-formaldehyde resins containing foaming agents with alkyl-aryl sulfonates present are commercially available, with one such material being sold under the code designation "Rapco Foam" by Raperswill Corporation of New York, N.Y. Other detergent-type foam-

ing agents may be utilized, a number of such materials being commercially available.

GENERAL COMMENTS

The improvement resulting from this change is a significant decrease in the time required for the partially cured foam to absorb a predetermined quantity of a soaking solution which contains both a nonionic and a cationic surfactant. It makes unnecessary a complex machine, the operation of which would require an employee with special training.

Since the active ingredient in the foaming agent is an anionic detergent, or surfactant, from the class of compounds with the general name alkyl-aryl sulfonate, and since it is known that the foam height such compounds can produce is increased on changing from tap water to distilled water, it appears quite likely that impurities in tap water inactivate a portion of the foaming agent. Certain cations present in tap water such as calcium, magnesium or iron can react with the active ingredient to form insoluble salts, much like the scum which results from using a soap in hard water. These insoluble salts can then be spread over the outer and inner surfaces of the foam structure, reducing the capacity of the foam to absorb the surfactants present in the soaking solution, or at least limiting the rate of this absorption.

In lieu of phosphoric acid set forth in the examples hereinabove, a water soluble acid may be used, including those water soluble acids selected from the group consisting of hydrochloric, benzene sulfonic and sulfuric acids.

Removal of these cationic impurities could improve the foam production process in two ways. First, by enhancing the efficiency of the foaming agent and secondly, by elimination of insoluble residues produced by their interaction with the foaming agent.

Also worthy of consideration is the fact that the soaking solution is now made with purified water whereas previously, it was made with tap water. The cationic surfactant contained in this solution may also react with anions such as fluoride, chloride, carbonate or sulfate, present in tap water, to produce insoluble residues which could interfere with absorption of the soaking solution by the foam in the same manner as has already been described.

In order to preserve the hydrophilic characteristics of the product, and in order to render the product more readily wettable, it may be desired to wet or soak the display blocks in water and package them in wet form. Such an arrangement would enable the consumer to more readily wet the product without delay. Normally, however, even dry floral display blocks prepared in accordance with the present invention may be utilized, since the hydrophilic qualities of the product render it quite readily wettable.

We claim:

1. The method of preparing hydrophilic floral display foam blocks of frothed urea-formaldehyde, wherein the urea-formaldehyde block comprises a solid frothed urea-formaldehyde resin with an alkyl-aryl sulfonate selected from the group consisting of sodium tertiary-butyl-benzene sulfonate, sodium hexylbenzene sulfonate, and sodium toluene sulfonate in an amount ranging from between 3.5% and 7% of the resin solids, phosphoric acid in an amount ranging from 10% to 20% of the resin solids; said method comprising:

(a) immersing said urea-formaldehyde resin block in an aqueous solution of a quaternary ammonium salt

selected from the group consisting of alkyltrimethylammonium chloride and dialkyldimethylammonium chloride wherein the alkyl portion of the compound has from between 8 and 18 carbon atoms, and wherein a molar concentration of quaternary ammonium salt is at least equal to the molar concentration of said alkyl-aryl sulfonate within the urea-formaldehyde resin.

2. The method of preparing hydrophilic floral display foam blocks of frothed urea-formaldehyde as defined in claim 1 being particularly characterized in that said alkyl-aryl sulfonate is 90% linear alkylate sulfonate-sodium salt.

3. The method as defined in claim 1 being particularly characterized in that said urea-formaldehyde resin contains starch.

4. The method as defined in claim 1 being particularly characterized in that sodium molybdate is present in said aqueous solution of quaternary ammonium salt.

5. Hydrophilic floral display foam blocks of frothed urea-formaldehyde resin, wherein said urea-formaldehyde resin block comprises:

(a) a frothed urea-formaldehyde resin block of substantially open cell configuration, said urea-formaldehyde resin block including:

(1) an alkyl-aryl sulfonate selected from the group consisting of sodium tertiary-butyl-benzene sulfonate, sodium hexylbenzene sulfonate, and sodium toluene sulfonate in an amount ranging from between about 3.5% and 7% of the resin solids;

(2) phosphoric acid in an amount ranging from between about 10% to 20% of the resin solids;

(3) a quaternary ammonium salt selected from the group consisting of alkyltrimethylammonium chloride and dialkyldimethylammonium chloride wherein the alkyl portion of the compound has from between 8 and 18 carbon atoms, and wherein said ammonium salt is present in substantially equal molar relationship to said alkyl-aryl sulfonate.

6. The hydrophilic floral display foam blocks of frothed urea-formaldehyde resin as defined in claim 5 wherein said urea-formaldehyde foam member contains starch in an amount ranging from about 5% to 15%.

7. The hydrophilic floral display foam blocks of frothed urea-formaldehyde resin as defined in claim 1 wherein the urea-formaldehyde block comprises a solid frothed urea-formaldehyde resin with a quaternary ammonium salt selected from the group consisting of alkyltrimethylammonium chloride and dialkyldimethylammonium chloride in an amount ranging between 3.5% and 7% of the resin solids; phosphoric acid in an amount ranging from 10% to 20% of the resin solids; said method comprising:

(a) immersing said urea-formaldehyde resin block in an aqueous solution of an alkyl-aryl sulfonate selected from the group consisting of sodium tertiary-butyl-benzene sulfonate, sodium hexylbenzene sulfonate, and sodium toluene sulfonate and wherein a molar concentration of alkyl-aryl sulfonate is at least equal to the molar concentration of said quaternary ammonium salt within the urea-formaldehyde resin.

8. The method as defined in claim 1 wherein the formal foam is shredded or changed in final shape or form to be utilized as a formal display material.

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9. Hydrophilic floral display foam blocks of frothed urea-formaldehyde resin, wherein said urea-formaldehyde resin block comprises:

(a) a frothed urea-formaldehyde resin block of substantially open cell configuration, said urea-formaldehyde resin block including:

(1) an alkyl-aryl sulfonate selected from the group consisting of sodium tertiary-butyl-benzene sulfonate, sodium hexylbenzene sulfonate, and sodium toluene sulfonate in an amount ranging from between about 3.5% and 7% of the resin solids;

(2) a water soluble acid selected from the group consisting of hydrochloric, benzene sulfonic and sulfuric acids;

(3) a quaternary ammonium salt selected from the group consisting of alkyltrimethylammonium chloride and dialkyldimethylammonium chloride wherein the alkyl portion of the compound has from between 8 and 18 carbon atoms, and wherein said ammonium salt is present in substantially equal molar relationship to said alkyl-aryl sulfonate.

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United States Patent [19]

[11] 4,225,679

Pilato

[45] Sep. 30, 1980

[54] **FLORAL FOAM PRODUCT AND METHOD OF PRODUCING THE SAME WHICH INCORPORATES A FLOWER PRESERVATIVE AND A BACTERIOCID**

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[52] **U.S. Cl.** 521/109; 71/68; 521/124; 521/128; 521/181

[58] **Field of Search** 71/68; 521/181, 109

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"The Greenhouse Environment" by J. W. Nastalerz, John Wiley & Sons (1977), pp. 573-580.

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[57] **ABSTRACT**

A foam product and method of producing the same for use in preserving cut flowers is provided which method provides in the manufacture of the product of foaming under mild conditions to preserve the wettability, and the preservative qualities of the foaming material and its additives so as to improve the life of the cut flowers which are mounted in the product.

5 Claims, No Drawings

FLORAL FOAM PRODUCT AND METHOD OF PRODUCING THE SAME WHICH INCORPORATES A FLOWER PRESERVATIVE AND A BACTERIOCID

This is a division of application Ser. No. 241, filed Jan. 2, 1979.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of producing a foam product and a product of the type which is made into blocks and into which cut flowers are pushed for support, transport and storage and use.

2. Description of the Prior Art

The use of phenol-formaldehyde (PF) or urea-formaldehyde (UF) foamed products as supports for cut flowers have been in common usage in the floral industry for many years. Either of the described foam products requires vigorous acid catalyzed conditions to transform the PF or UF resin (with surfactant, wetting agent, blowing agent, and color) into foam which foam may vary in density from 1.0 to 2.0 lb./ft³. A low density foam product is desirable for fragile flowers while a higher density foam product is suitable for heavy flowers or dry flowers. Foam properties desired are rapid wettability, good water retention, proper color, a crisp texture and ease of flower penetration, with good support and retention of the flower stems by the foam. The usual practice is to add a flower preservative to the water which the foams imbibe.

The U.S. Pat. to Smithers, No. 2,753,277 describes an absorbent material for floral arrangements wherein the foam is provided with a layer of wetting agent on the exterior to carry water into the interior of the foam mass. The foaming process is described as vigorous, and would deteriorate the flower preservative and bactericide.

The U.S. Pat. to Palombo, No. 3,049,444 discloses a foamed cellular synthetic material impregnated with a wetting agent and wherein the foam mass is provided with interior passages with a wetting agent disposed along the passages. The process has the same adverse affects as Smithers.

The U.S. Pat. to Jackson, Jr., No. 3,101,242 discloses a process of making flexible absorbent material wherein the foam mass prepared in accordance with Smithers U.S. Pat. No. 2,753,277 is compressed, bleached, leached to remove water soluble chemicals and treated with a wetting agent to increase its absorptive capacity.

The U.S. Pat. to Palombo, No. 3,697,457 describes a self wetting phenolic foam product wherein when making the foamed product, the wetting agents are mixed with the resin prior to foaming in separate additions to obtain faster wetting and maximum water absorption in the foamed product.

The foaming condition as described for these prior art foam products including those disclosed by Smithers, the Palombo patents and Jackson are severe and decompose or char many flower preservatives, such as bactericides, sucrose, glucose and the like which would be incorporated into the resin prior to foaming.

The process for producing my foam product takes place under mild foaming conditions wherein sucrose, glucose and other saccharidic materials as well as bactericides can be introduced into the resin prior to foaming. The foam appearance of the newly discovered

composition in the absence of color additives exhibits no evidence of charring or decomposition of the preservative additive. The unusually mild foaming condition of my process, namely low concentration of acid catalyst, and longer curing time are beneficial in the preparation of a new floral foam composition with preservatives carried thereby. The desired product is described in "The Greenhouse Environment" by J. W. Mastalers, John Wiley & Sons (1977) at pp. 573-580.

SUMMARY OF THE INVENTION

A floral foam product and method of producing the same are disclosed which have incorporated therein and contains a flower preservative and a bactericide which is not adversely affected by the foaming process which produces the foamed product.

The principal object of the invention is to provide a foam product and method of making the product which product contains a flower preservative, bactericide and has high water retention.

It is a further object of the invention to provide a foam product and a method of producing the foam product that is simple and inexpensive.

Other objects and advantageous features of the invention will be apparent from the description and claims.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the invention, the method of producing the foamed product and the product can be accomplished by selecting a phenolic resin of low viscosity in the range of 1000 to 2000 CPS at ambient or room temperature which aids in dissolving the flower preservative as described below.

A flower preservative additive in the range of 1-10% with the preferred range of 2-5% is selected such as sucrose, glucose, fructose or other mono-, di- and trisaccharides which are water soluble or water dispersible.

A suitable bactericide is selected such as silver nitrate or acetate, 8-hydroxy quinoline nitrate or acetate, or sodium benzoate at a concentration of 10-200 PPM in an aqueous solution.

A preferred embodiment is given in the following example in which the quantities are stated in parts by weight.

Resin Formulation Components	Composition
Phenolformaldehyde Resin GH 278	76-83
Surfactant (Tween 40 or 60) (polyoxyethylene sorbitan monolaurate)	3-4
Wetting Agent (Texapon N-25)	3-4
Pentane (blowing agent)	4-5
Urea	1
Preservative, such as sucrose, glucose	2-5
Phenol Sulfonic Acid Catalyst	4-5
Bactericide, such as silver nitrate	10-200 ppm
Color	0.5

In preparing the foam product the phenolic resin, surfactant, wetting agent, urea (to reduce formaldehyde odor) preservative, bactericide and color are mixed at room temperature or 72° to 75° F. After a few minutes pentane is added to the mixture followed by the addition of the acid catalyst.

The resulting mixture is then poured into a mold which has been pre-heated to a temperature of 110° to

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120° F. and allowed to sit for 30-60 minutes, the mold is placed into an oven and the foam expanded to its maximum height, at a temperature range of 110° to 120° F. The foam product is removed from the mold and cut into 9 inch x 3.25 inch x 4.25 inch size bricks for insertion of cut flowers.

While other suitable resins can be utilized the resin example given in the example is particularly suitable.

I claim:

1. The method of producing a foamed product of the type useful for floral displays which method comprises mixing at ambient temperature a phenol formaldehyde resin having a viscosity of 1000 to 2000 CPS with soluble additives comprising
 - a surfactant,
 - a wetting agent,
 - a flower preservative selected from the group consisting of water soluble or dispersible saccharides, and
 - a bactericide,adding a foaming agent to the mixture, then adding a catalyst to the mixture,

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delivering the aforesaid mixture into a preheated mold and retaining it in the mold for a period of about 30 to 60 minutes,

heating the mold and its contents to foam the mixture in the mold for maximum foam formation, and removing the foamed material from the mold for use.

2. A method of producing a foamed product as defined in claim 1 in which

said flower preservative is from the group consisting of sucrose, glucose, fructose, mono-saccharides, di-saccharides and tri-saccharides.

3. A method as defined in claim 1 in which said flower preservative is in the range of from 1 to 10% by weight.

4. A method of producing a foamed product as defined in claim 1 in which

the bactericide is from the group consisting of silver nitrate, silver acetate, 8-hydroxy quinoline nitrate, 8-hydroxy quinoline acetate, and sodium benzoate.

5. A method as defined in claim 4 in which the bactericide is in the range of 10 to 200 ppm.

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 suitable organic compound which contains a radical equivalent of the substituted radical. The phenolic resin may contain free hydroxy, epoxy and mixture thereof. Most of the epoxy radicals are converted to hydroxy radicals.

The preferred method used to produce tough, solid thermoplastic phenolic resin is to mix simultaneously equal mol-equivalents of the reactants, substituted organic compound containing hydroxy or epoxy radical, phenol-type compound, and alkali salt-forming compound, then subject the mixture, keeping the temperature between 87° C. to 120° C. for 1 to 10 hours, thereby producing a phenolic resin.

Thermosetting phenolic resin may be produced by using cross-linking compounds, such as adding a 15 different compound, e.g., polyphenyl polyepoxy, chlorobiphenyl with an epichlorohydrin, aldehydes, etc. Phenolic resin solid and cellular products are produced by mixing and reacting the following compounds:

- A. Substituted organic compound containing hydroxy radical, epoxy radical, or mixtures thereof, in the amount of 10 to 100 parts by weight.
- B. Phenol-type compounds in the amount of 10 to 50 parts by weight.
- C. Alkali salt-forming compound in an amount of 1 to 50 parts by weight.

Component A

Any suitable organic compound which contains a 30 substituent that will react with the alkali salt-forming compound and contains a radical that will react with the phenol-type compound may be used in this invention. The substituents can be halogen, acid sulfate, nitrate, acid phosphate, bicarbonate, carbonate, acid malonate, acid succinate, acid citrate, and others. The substituted organic compound should contain a hydroxy radical, epoxy radical, or mixtures thereof. Organic compounds containing a halogen radical and an epoxy or hydroxy radical are preferred, e.g., a polyfunctional halohydrin. Organic halohydrins such as epichlorohydrin, dibromohydrin, diiodohydrin or other halohydrins derived from glycerol in which one terminal hydroxy group is replaced by one or two halogen atoms, e.g., by chlorine, bromine, iodine or others 45 which may react with an alkali group to produce an epichlorohydrin, and mixtures thereof, may be used. Organic esters and ether wherein the hydroxy portion is substituted with a radical that will react with the 50 alkali salt-forming compound, e.g., dichloroethyl ether, may be used.

Any poly-substituted organic compound which is converted with a substituted organic compound with a hydroxy radical or an epoxy radical during the course 55 of the reaction of the components in this invention, e.g., ethylene dichloride, undergoes hydrolysis in the presence of sodium carbonate and water. Glyceryl dichloride is converted to epichlorohydrin in the presence of an alkali metal compound, propylene chlorohydrin is converted to propylene oxide, and ethylene chlorohydrin is converted to ethylene oxide in the presence of an alkali metal compound. Hydrolysis of alkyl polyhalides and polyhaloether halides with aqueous alkali metal hydroxides and various organic alkalies may be 65 hydrolyzed to aldehydes or ketones, polyester compounds, substituted esters when an alcohol portion is substituted, polyester resins, polyvinyl acetate, polyvinyl

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hydroxy organic phosphates, may be used in this invention.

Compounds which contain a substituted and an epoxy radical, e.g., substituted propylene oxide, substituted butylene oxide may be used in this invention.

Compounds which contain a substituent and a hydroxy radical, e.g., ethylene chlorohydrin, substituted methanol, substituted propanol, chloroethoxy ethylene, substituted ethanol, etc., may be used in this invention.

Substituted organic compounds may contain a hydroxy radical or epoxy radical and have the general formula of:



where R is a carbon atom or an organic group, saturated or unsaturated, preferably an aliphatic group where R' is the same or different organic radical or hydrogen. Preferably, the R' group may, for example, be CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_6H_{13} , C_8H_{17} , $\text{C}_{10}\text{H}_{21}$, $\text{C}_{12}\text{H}_{25}$, $\text{C}_{14}\text{H}_{29}$, $\text{C}_{16}\text{H}_{33}$, $\text{C}_{18}\text{H}_{37}$, $\text{C}_{20}\text{H}_{41}$, $\text{C}_{22}\text{H}_{45}$, $\text{C}_{24}\text{H}_{49}$, $\text{C}_{26}\text{H}_{53}$, $\text{C}_{28}\text{H}_{57}$, $\text{C}_{30}\text{H}_{61}$, $\text{C}_{32}\text{H}_{65}$, $\text{C}_{34}\text{H}_{69}$, $\text{C}_{36}\text{H}_{73}$, $\text{C}_{38}\text{H}_{77}$, $\text{C}_{40}\text{H}_{81}$, $\text{C}_{42}\text{H}_{85}$, $\text{C}_{44}\text{H}_{89}$, $\text{C}_{46}\text{H}_{93}$, $\text{C}_{48}\text{H}_{97}$, $\text{C}_{50}\text{H}_{101}$, $\text{C}_{52}\text{H}_{105}$, $\text{C}_{54}\text{H}_{109}$, $\text{C}_{56}\text{H}_{113}$, $\text{C}_{58}\text{H}_{117}$, $\text{C}_{60}\text{H}_{121}$, $\text{C}_{62}\text{H}_{125}$, $\text{C}_{64}\text{H}_{129}$, $\text{C}_{66}\text{H}_{133}$, 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$\text{C}_{316}\text{H}_{633}$, $\text{C}_{318}\text{H}_{637}$, $\text{C}_{320}\text{H}_{641}$, $\text{C}_{322}\text{H}_{645}$, $\text{C}_{324}\text{H}_{649}$, $\text{C}_{326}\text{H}_{653}$, $\text{C}_{328}\text{H}_{657}$, $\text{C}_{330}\text{H}_{661}$, $\text{C}_{332}\text{H}_{665}$, $\text{C}_{334}\text{H}_{669}$, $\text{C}_{336}\text{H}_{673}$, $\text{C}_{338}\text{H}_{677}$, $\text{C}_{340}\text{H}_{681}$, $\text{C}_{342}\text{H}_{685}$, $\text{C}_{344}\text{H}_{689}$, $\text{C}_{346}\text{H}_{693}$, $\text{C}_{348}\text{H}_{697}$, $\text{C}_{350}\text{H}_{701}$, $\text{C}_{352}\text{H}_{705}$, $\text{C}_{354}\text{H}_{709}$, $\text{C}_{356}\text{H}_{713}$, $\text{C}_{358}\text{H}_{717}$, $\text{C}_{360}\text{H}_{721}$, $\text{C}_{362}\text{H}_{725}$, $\text{C}_{364}\text{H}_{729}$, $\text{C}_{366}\text{H}_{733}$, $\text{C}_{368}\text{H}_{737}$, $\text{C}_{370}\text{H}_{741}$, $\text{C}_{372}\text{H}_{745}$, $\text{C}_{374}\text{H}_{749}$, $\text{C}_{376}\text{H}_{753}$, 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lized and stabilized by additions such as metallic powders, ethyl cellulose, chlorinated natural rubber, polyvinyl acetate, polyvinyl chlorides, metallic oxides and hydroxides alkylated phenacyl compounds, polyethoxy ethanol, sodium diethyl sulfosuccinate, diethyl calcium sulfosuccinate, diethyl sulfosuccinate, methyl morpholine, diethylmorpholine, polyether siloxanes, and mixtures thereof.

Various phenolic resins are utilized as hot-melt adhesive, various additives may be added such as tougheners, reinforcing agents, viscosity controller, plasticizer, color pigment, fillers, etc.

[illegible]

with metal, glass, plastic, wood or concrete. If desired, these sandwich elements may be flamed. These products may be used as hollow bodies, e.g., as formers for goods which may be required to be moist or cool, as filter materials or exchangers, as catalyst carriers or as carriers of active substances, as desiccative elements, furniture components and filling for cavities. They may be found in the field of model building and model building, and in the production of molds for metal castings, which may also be considered.

Fillers in the form of powders, granules, wire, fibers, dumb-bell-shaped particles, crystallites, strands, rods, beads, hollow beads, foam particles, non-woven webs, fibers, and fibers with cross-sections of various shapes, in place of or woven or knitted fabrics, tapes and pieces of fabric or solid or organic substances, e.g., dolomite, chalk, alumina, asbestos, basic silicic acids, sand, iron oxide, aluminum oxide and hydroxide, calcium silicates, aluminum silicates, basalt wool or powder, glass fibers, carbon fibers, graphite, carbon black, Al₂O₃, Cu and Cu oxides, molybdenum disulfide, steel

wood, bronze or copper meshes, silicon powder, expanded clay particles, hollow glass beads, glass powder, lava and pumice particles, wood chips, wood meal, cork, cotton, straw, popcorn, coke or purities of filled or unfilled, foamed or unfoamed, stretched or unstretched organic polymers, may be added to the mixture of the components in many emulsification. Aqueous

[illegible]

The composite materials of the invention may be mixed with considerable quantities of fillers without losing their advantageous properties and, in particular, the composite materials which consist predominantly of organic constituents which are, preferably, filled with inorganic fillers.

Blowing agents may be used in this invention. The blowing agents are usually inert liquids with boiling points ranging from -25° to 80° C. The organic blowing agents may be, e.g., acetone, ethyl acetate, halogenated alkanes, e.g., methyl acetate, methyl formate, methyl acetate, dichloromethane, butane, hexane, heptane or dichlorofluoromethane. There are compounds which decompose at temperatures above room temperature with liberation of, e.g., nitrogen. Compressed air, nitrogen or carbon dioxide may also be used as the blowing agent. Steam may be used as the blowing agent. The reaction products of diethylenetriamine and isocyanate compounds, when heated to above 80° C., liberate steam which may be used as the blowing agent.

The novel cellular and solid products produced by this invention have many uses. The reaction mixtures, with a blowing agent, may be mixed in a mixing apparatus, then the reaction mixture may be sprayed by means of compressed air or by the airless spraying process onto various surfaces. Subsequently, the mixture expands and fills the voids in the surface. The reaction mixture is in the form of a cellular solid which is useful for insulation, cavity filling and coating. The reaction mixture may also be forced, poured or injected into mold or

There may also be towers, pipes or apparatus used to cast heated molds, optionally by centrifugal casting, and left to harden at room temperature or at temperatures up to 120°C, optionally under pressure. Reinforcing elements may quite easily be incorporated into the reaction mixtures. These products may also be used as cavity fillings, packaging materials, building materials, e.g. lightweight building bricks and panels, having a good solvent resistance, advantageous fire-resistant characteristics, good strength, high dimensional stability and good weather resistance.

Any suitable compound containing two or more isocyanate groups may be used to react with the phenolic resins produced by the process of this invention. Suitable organic polyisocyanates include aliphatic, cycloaliphatic and aromatic polyisocyanates.

The formula may be crushed and used for propagation of seedlings, cuttings and plants or cut flowers after washing out any salt.

$O=C-N-R-N=C=O$

wherein R is a divalent organic radical such as an alkylene, aralkylene or arylene.

triphenylmethane-4,4',4''-trisulfonates, polychlorophenylmethanes, polycyclohexylmethanes, and the like, which may be obtained by sulfonation of the corresponding aromatic hydrocarbons, and by acid-catalyzed condensation followed by phosgene reaction, to form substituted cyclohexylmethanes, and by phosgene reaction of cyclohexylmethanes, instead of acid-catalyzed condensation, to form substituted cyclohexylmethanes in acetoacetic polymerization of the type described in the foregoing. The production of tolylene diisocyanate in the commercial production of tolylene diisocyanate, and the production of tolylene diisocyanate, diphenylmethane diisocyanates, or hexamethylene diisocyanate, modified polyisocyanate, or cyclohexylmethane diisocyanate, or mixtures thereof may be used in the invention.

Any scitible polycarboxylic acid or polycarboxylic acid anhydride may be used in this invention to modify the phenolic resin or to react with the phenolic resin to produce phenolic polyester resins.

Malic acid, sebacic acid, phthalic acid, isophthalic acid, trimellitic acid, fumaric acid, maleic acid, oxalic acid, succinic acid, and trimellitic anhydride and mixtures thereof.

Suitable polycarboxylic acid and anhydrides include, but are not limited to, phthalic anhydride, tetraphthalic anhydride, trimellitic anhydride, maleic anhydride and mixtures thereof.

Any suitable oils, such as drying oils, may be used in this invention to modify the phenolic resin. Suitable oils include, but are not limited to, linseed oil, dehydrated castor oil, peanut butter, etc. The phenolic resin may be used as coating agents, casting material, further reacted with polyisocyanates, etc.

castor oil, soya bean oil, cornstepped oil, tall oil, fish oil, linseed oil, tung oil, coconut oil, castor oil, rapeseed oil, perilla oil, cod liver oil, sunflower oil, safflower oil, walnut oil, and mixtures thereof. These modified phenolic resins may be used as coating agents.

The ratio of the essential reactants and optional reactants which lead to the phenolic solid or foamed product of this invention vary, broadly speaking, within ranges as follows:

10 to 100 parts by weight of Component A (resin-

- (b) 10 to 50 parts by weight of Component A (phosphoric acid);
- (c) 10 to 50 parts by weight of Component B (phosphate compound);
- (d) 10 to 50 parts by weight of Component C (alkali salt-forming compound);
- (e) 10 to 50 parts by weight of Component D (modifying compound).

(e) up to 20% by weight, based on weight of Components A, B and C, of a foam stabilizer;

(f) up to 10% by weight, based on weight of Components A, B and C, of an emulsifier;

(g) up to 300% by weight, based on weight of Components A, B and C, of inert filler material;

(h) 1 to 100 parts by weight of an organic isocyanate compound with 2 or more isocyanate radicals, reacted with 20 to 50 parts by weight of phenolic resin, weighed in to the parts by weight.

(1) 1 to 100 parts by weight of an organic polycarbonic acid or anhydride reacted with 20 to 50 parts by weight of phenolic resin produced in this invention;

(2) 1 to 10 parts by weight of polyamine to 2 to 15 parts by weight of an epichlorohydrin;

The object of the present invention is to provide a novel process to produce phenolic resin solid and foam products. Another object is to produce novel solid and foam products from a mixture of formaldehyde and urea foamed products. Another object is to produce novel cellular and solid phenolic resins which are relatively low cost. Still another object is to produce novel fine cellular products which are relatively low in cost. In short, light-weight, high-strength fire-resistant, tough, rigid, light-weight, high-strength, fire-resistant, good resistance and dimensional stability and are useful

Good resistance and dimensional stability are an essential feature of many of the plastics used for thermal and sound insulation, shock-resistant packaging, as a coating agent, adhesive, casting material, cavity fillers, etc. Another object is to produce solid phenolic resins which may be utilized as a hot-melt adhesive, coating agent, molding powder, casting material, cavity filler, etc.

DESCRIPTION OF PREFERRED EMBODIMENTS

My invention will be illustrated in greater detail by the specific Examples which follow, it being understood that these preferred embodiments are illustrative of, but not limited to, procedures which may be used in the production of phenolic resin products. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

About 60 parts of phenol, 60 parts by weight of opocetyl alcohol, and 40 parts by weight of caustic soda (NaOH) are mixed, then agitated, keeping the temperature below the boiling point of the reactants. The reaction is exothermic for about 30 minutes, then the mixture is heated to 80°C . to 120°C . for 12 hours, thereby producing a solid water-colored thermoplastic phenolic resin. The resin is washed in hot dilute hydrochloric acid. The resin is not water-soluble. The resin softens at about 68°C . and melts at 80°C . to 100°C . It has very good adhesive properties, is flexible, has good thermal resistance, and is soluble in phenetic etheralcoholin, benzene chloroform and other aromatic solvents.

EXAMPLE 2

[illegible]

EXAMPLE 3

[illegible]

EXAMPLE 4

About 60 parts by weight of phenol, 20 parts by weight of ethylene chlorohydrin, 40 parts by weight of calcium chloride, and 40 parts by weight of caustic soda are mixed, then agitated, keeping the temperature below the boiling point of the reactants. The reaction is exothermic for about 30 minutes, then the mixture is heated to 80° C. to 120° C. for 1 to 12 hours, thereby producing a tan-colored, solid phenolic resin. The resin becomes thermosetting on further heating. It may be used as molding material.

EXAMPLE 4

About 60 parts by weight of phenol, 20 parts by weight of epichlorohydrin, 40 parts by weight of epichlorohydrin and 40 parts by weight of caustic soda are mixed, then agitated while keeping the temperature below the boiling point of the reactants. The reaction is exothermic for about 30 minutes. The temperature is kept between 80° C. to 120° C. for 1 to 12 hours, thereby producing a thick liquid phenolic resin.

The reaction is exothermic for about 30 minutes, then the mixture is heated to 80° C. to 120° C. for 1 to 12 hours, thereby producing a resinsoluble, solid phenolic resin. The resin becomes thermosetting on further heating. It may be used as molding material.

EXAMPLE 5

About one mol of trichloroethylene oxide, one mol of phenol and one mol of sodium hydroxide are mixed, then agitated while keeping the temperature between 80° C. to 120° C. for 1 to 12 hours, thereby producing a solid brown-colored, thermoplastic phenolic resin.

EXAMPLE 6

About one mol of a substituted compound selected from the list below, one mol of phenol and one mol of sodium hydroxide (caustic soda) are mixed, then agitated while keeping the temperature between 80° C. to 120° C. for 1 to 12 hours, thereby producing a solid phenolic resin.

- (a) propylene chlorohydrin;
- (b) ethylene bromohydrin;
- (c) glyceryl monofluoride;
- (d) glyceryl mono-oxide;
- (e) glyceryl monosulfate;
- (f) glyceryl monosulfate;
- (g) ethylene carbonate;
- (h) ethylene carbonate;
- (i) trichloroethylene oxide;
- (j) trichloroethylene oxide;
- (k) trichloroethylene oxide;
- (l) 2,3-dibromopropanol;
- (m) chloroacetyl phosphate ester;
- (n) polyether phosphate polyol (VIRCOL 82 produced by Mobel);
- (o) 3 mols of propylene glycol reacted with one mol of phosphoric acid;
- (p) aromatic polyester polyol (TETRA 202 by Hercules, Inc.);
- (q) nitrocellulose;
- (r) nitrocellulose;
- (s) nitrocellulose;
- (t) dichlorodimethyl ether;
- (u) polyvinyl acetate emulsion;
- (v) mixtures thereof.

EXAMPLE 7

EXAMPLE one is modified wherein 10 parts by weight of cresol are used in place of 10 parts by weight of phenol and used with the phenol, thereby producing a phenolic epoxy resin.

EXAMPLE 8

EXAMPLE one is modified wherein 10 parts by weight of cresol are used in place of 10 parts by weight of phenol and used with the phenol, thereby producing a phenolic resin.

EXAMPLE 9

About 25 parts by weight of resorcinol, 25 parts by weight of phenol, 60 parts by weight of epichlorohydrin

and 40 parts by weight of caustic soda (NaOH) are mixed, then agitated while keeping the temperature below the boiling point of the reactants. The reaction is exothermic for about 30 minutes. The temperature is kept between 80° C. to 120° C. for 1 to 12 hours, thereby producing a thick liquid phenolic resin.

EXAMPLE 10

About 30 parts by weight of phenol, 60 parts by weight of epichlorohydrin and 40 parts by weight of caustic soda (NaOH) are mixed, then agitated while keeping the temperature below the boiling point of the reactants. The reaction is exothermic for about 30 minutes. The temperature is kept between 80° C. to 120° C. for 1 to 12 hours, thereby producing a liquid phenolic resin.

EXAMPLE 11

Example 2 is modified wherein 10 parts by weight of epichlorohydrin and 40 parts by weight of caustic soda (NaOH) are substituted for 10 parts by weight of caustic soda and used with the caustic acid, thereby producing a phenolic compound.

EXAMPLE 12

About 30 parts by weight of phenol, 10 parts by weight of a polyether diol or glycol, selected from the list below, 60 parts by weight of epichlorohydrin, and 40 parts by weight of caustic soda (NaOH) are mixed, then agitated, keeping the temperature below the boiling point of the reactants. The reaction is exothermic for about 30 minutes, then the mixture is kept at a temperature of 80° C. to 120° C. for 1 to 12 hours, thereby producing a phenolic compound.

- (a) ethylene glycol;
- (b) propylene glycol;
- (c) glycerol;
- (d) glycerol;
- (e) diethylene glycol;
- (f) triethylene glycol;
- (g) polypropylene glycol;
- (h) butane diol;
- (i) triethylene glycol;
- (j) tetraethylene glycol;
- (k) hexane 1,6-diol;
- (l) diethylene glycol;
- (m) trichloro-1,1-dihydroxy ethane;
- (n) mixture of the above.

EXAMPLE 13

EXAMPLE 12 is modified wherein another organic polyol is used in place of the organic diol and is selected from the list below:

- (a) glycerol;
- (b) trimethylol propane;
- (c) sucrose;
- (d) carboxylates;
- (e) starch;
- (f) castor oil;
- (g) cellulose;
- (h) butane-1,4-triol;
- (i) glucose;
- (j) castor oil (triol);
- (k) pentaerythritol;
- (l) polyester polyols;
- (m) polypropylene triol, 1000 molecular weight;
- (n) polyethylene triol, 1500 molecular weight.

EXAMPLE 14

About 10 parts by weight of phenol and 20 parts by weight of epichlorohydrin are mixed, then 10 parts by weight of caustic soda (NaOH) are slowly added while agitating and the temperature is kept between 80° C. and 120° C. for about 1 to 12 hours. A tan solid phenolic resin is produced which is thermosetting.

EXAMPLE 15

About 10 parts by weight of phenol, 20 parts by weight of epichlorohydrin and 5 parts by weight of an alkali salt-forming compound, selected from the group below, are mixed and then agitated while keeping the temperature below the boiling point of the reactants for 1 to 12 hours, thereby producing a liquid phenolic resin with free epoxy radicals and hydroxyl radicals. The resin may be reacted with polyisocyanates to produce foam products.

- (a) caustic soda ($\text{NaOH} \cdot 3\text{H}_2\text{O}$);
- (b) sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$);
- (c) sodium bicarbonate;
- (d) potassium carbonate;
- (e) potassium carbonate ($\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$);
- (f) sodium hydroxide;
- (g) calcium hydroxide.

EXAMPLE 16

Example 15 is modified wherein 10 parts by weight of the alkali salt-forming compound are used in place of 5 parts by weight of the alkali salt-forming compound, thereby producing a liquid phenolic resin with free epoxy and hydroxyl radicals.

EXAMPLE 17

About 20 parts by weight of cresylic acid and 10 parts by weight of caustic soda are mixed and reacted. Then this mixture is slowly added to 40 parts by weight of epichlorohydrin while agitating and keeping the temperature between 50° C. to 80° C. for about 1 hour, thereby producing a liquid phenolic resin with free epoxy and hydroxyl radicals. This resin may be used for the polyol in production of polyurethane foams and resins.

EXAMPLE 18

EXAMPLE 17 is modified wherein 20 parts by weight of an organic compound, selected from the list below, are added with the components, thereby producing a modified phenolic resin.

- (a) ethylene chlorohydrin;
- (b) propylene chlorohydrin;
- (c) methylacrylic acid;
- (d) acrylic acid;
- (e) crotonic acid;
- (f) phthalic anhydride;
- (g) maleic acid;
- (h) sodium adipate;
- (i) potassium succinate;
- (j) sodium succinate;
- (k) sodium polycarbonate;
- (l) methyl mercaptan;
- (m) vinyl acetate;
- (n) acrylonitrile;
- (o) acrylonitrile;
- (p) acrylonitrile;
- (q) acrylonitrile;
- (r) methacrylate;
- (s) methacrylate;
- (t) methacrylate;
- (u) methacrylate;
- (v) methacrylate;
- (w) methacrylate;
- (x) methacrylate;
- (y) methacrylate;
- (z) methacrylate;

- (a) aniline;
- (b) phenylacetamide;
- (c) ethylene dichloride;
- (d) castor oil;
- (e) diiodine diethyl silane;
- (f) cresyl phosphate.

EXAMPLE 19

About 10 parts by weight of phenol, 5 parts by weight of a polyfunction phenol-type compound, selected from the list below, were mixed and 20 parts by weight of epichlorohydrin and 10 parts by weight of caustic soda granules were slowly added while agitating and keeping the temperature at 80° C. to 120° C. for 1 to 12 hours, thereby producing a thermosetting phenolic resin.

- (a) resorcinol;
- (b) Bisphenol A;
- (c) Phenol novolac;
- (d) triphenyl methane;
- (e) methylene dianiline;
- (f) 4-aminophenol;
- (g) 4-aminophenol;
- (h) 4-aminophenol;
- (i) 4-aminophenol;
- (j) 4-aminophenol;
- (k) 4-aminophenol;
- (l) 4-aminophenol;
- (m) 4-aminophenol;
- (n) 4-aminophenol;
- (o) 4-aminophenol;
- (p) 4-aminophenol;
- (q) 4-aminophenol;
- (r) 4-aminophenol;
- (s) 4-aminophenol;
- (t) 4-aminophenol;
- (u) 4-aminophenol;
- (v) 4-aminophenol;
- (w) 4-aminophenol;
- (x) 4-aminophenol;
- (y) 4-aminophenol;
- (z) 4-aminophenol;

EXAMPLE 20

EXAMPLE 19 is modified wherein the phenolic resin is washed in hot dilute acid or neutral chloride, selected from the list below, thereby removing the salt and lowering the pH.

- (a) hydrochloric acid;
- (b) sulfuric acid;
- (c) nitric acid;
- (d) acetic acid;
- (e) magnesium chloride;
- (f) aluminum chloride.

EXAMPLE 21

EXAMPLE 19 is modified when 5 parts by weight of an aldehyde, selected from one group below, are mixed into the melted phenolic resin produced in EXAMPLE 1, thereby producing a modified phenolic resin.

- (a) formaldehyde;
- (b) acetaldehyde;
- (c) butyraldehyde;
- (d) ethanal;
- (e) acetone;
- (f) formalin;
- (g) formalin;
- (h) formalin;
- (i) formalin;
- (j) formalin;
- (k) formalin;
- (l) formalin;
- (m) formalin;
- (n) formalin;
- (o) formalin;
- (p) formalin;
- (q) formalin;
- (r) formalin;
- (s) formalin;
- (t) formalin;
- (u) formalin;
- (v) formalin;
- (w) formalin;
- (x) formalin;
- (y) formalin;
- (z) formalin;

EXAMPLE 22

About 40 parts by weight of phenol, 60 parts by weight of epichlorohydrin, 20 parts by weight of an oil, selected from the list below, and 30 parts by weight of caustic soda are mixed, then agitated while keeping the temperature below the boiling point of the reactants for 1 to 12 hours, thereby producing a modified phenolic resin. This resin may be used as a coating agent.

- (a) linseed oil;
- (b) dehydrated castor oil;
- (c) soybean oil;
- (d) cottonseed oil;
- (e) tall oil;
- (f) tall oil;
- (g) tall oil;
- (h) tall oil;
- (i) tall oil;
- (j) tall oil;
- (k) tall oil;
- (l) tall oil;
- (m) tall oil;
- (n) tall oil;
- (o) tall oil;
- (p) tall oil;
- (q) tall oil;
- (r) tall oil;
- (s) tall oil;
- (t) tall oil;
- (u) tall oil;
- (v) tall oil;
- (w) tall oil;
- (x) tall oil;
- (y) tall oil;
- (z) tall oil;

- (f) citric acid;
(g) malic acid;
(h) tartaric acid;
(i) succinic acid;
(j) fumaric acid;
(k) maleic acid;
(l) phthalic acid;
(m) isophthalic acid;
(n) terephthalic acid;
(o) trimellitic acid;
(p) pyromellitic acid;
(q) trimellitic anhydride;
(r) pyromellitic anhydride;
(s) trimellitic anhydride;
(t) pyromellitic anhydride;
(u) trimellitic anhydride;
(v) pyromellitic anhydride;
(w) trimellitic anhydride;
(x) pyromellitic anhydride;
(y) trimellitic anhydride;
(z) pyromellitic anhydride.

EXAMPLE 23

About 100 parts by weight of the phenolic resin produced in EXAMPLE 22 are mixed with 25 parts by weight of a filler, listed below, then heated to melt the resin and then pressed in a mold under pressure, thereby producing a modified phenolic resin product.

- (a) wood flour;
(b) wood fibers;
(c) cotton fibers;
(d) glass fibers;
(e) asbestos;
(f) mica;
(g) diatomaceous earth;
(h) silica powder;
(i) metal fibers;
(j) graphite;
(k) metal powder;
(l) metal oxides;
(m) carbon;
(n) carbon fibers;
(o) fibers;
(p) fibrous materials;
(q) mineral fibers;
(r) mineral fibers;
(s) mineral fibers;
(t) mineral fibers;
(u) mineral fibers;
(v) mineral fibers;
(w) mineral fibers;
(x) mineral fibers;
(y) mineral fibers;
(z) mineral fibers.

EXAMPLE 24

About equal parts by weight of the phenolic resin produced in EXAMPLE 17 and a polyisocyanate compound, selected from the list below, were mixed and reacted, thereby producing a foamed polyurethane product.

- (a) toluene-2,4- and -2,6-diisocyanate;
(b) polyphenyl-polyphenyl-diisocyanate, obtained by nitric-formaldehyde condensation followed by polycondensation;
(c) hexamethylene diisocyanate;
(d) isophorone diisocyanate;
(e) perfluorinated diisocyanate;
(f) 1,4-bis(isocyanatophenyl) ether;
(g) 4,4'-biphenyl diisocyanate;
(h) 4,4'-oxydiphenyl diisocyanate;
(i) 4,4'-methylenediphenyl diisocyanate;
(j) 4,4'-methylenediphenyl diisocyanate;
(k) 4,4'-methylenediphenyl diisocyanate;
(l) 4,4'-methylenediphenyl diisocyanate;
(m) 4,4'-methylenediphenyl diisocyanate;
(n) 4,4'-methylenediphenyl diisocyanate;
(o) 4,4'-methylenediphenyl diisocyanate;
(p) 4,4'-methylenediphenyl diisocyanate;
(q) 4,4'-methylenediphenyl diisocyanate;
(r) 4,4'-methylenediphenyl diisocyanate;
(s) 4,4'-methylenediphenyl diisocyanate;
(t) 4,4'-methylenediphenyl diisocyanate;
(u) 4,4'-methylenediphenyl diisocyanate;
(v) 4,4'-methylenediphenyl diisocyanate;
(w) 4,4'-methylenediphenyl diisocyanate;
(x) 4,4'-methylenediphenyl diisocyanate;
(y) 4,4'-methylenediphenyl diisocyanate;
(z) 4,4'-methylenediphenyl diisocyanate.

EXAMPLE 25

EXAMPLE 24 is modified wherein up to 20% by weight of a foam stabilizer up to 15% by weight of an organotin catalyst up to 10% by weight of an amine catalyst up to 5% by weight of a blowing agent, and up to 10% by weight of a retarder are added to the resin mixture of EXAMPLE 24. Percentages are based on the weight of the resin mixture.

EXAMPLE 26

EXAMPLE 1 is modified by adding 20 parts by weight of a polyisocyanate compound or anhydride, selected from the list below, to 100 parts by weight of the modified phenolic resin produced in EXAMPLE 1. The mixture is heated at 80° C. to 120° C. for 1 to 12 hours, thereby producing a modified phenolic resin.

- (a) isocyanic acid;

- (b) acetic acid;
(c) malic acid;
(d) tartaric acid;
(e) succinic acid;
(f) fumaric acid;
(g) maleic acid;
(h) phthalic acid;
(i) isophthalic acid;
(j) terephthalic acid;
(k) trimellitic acid;
(l) pyromellitic acid;
(m) trimellitic anhydride;
(n) pyromellitic anhydride;
(o) trimellitic anhydride;
(p) pyromellitic anhydride;
(q) trimellitic anhydride;
(r) pyromellitic anhydride;
(s) trimellitic anhydride;
(t) pyromellitic anhydride;
(u) trimellitic anhydride;
(v) pyromellitic anhydride;
(w) trimellitic anhydride;
(x) pyromellitic anhydride;
(y) trimellitic anhydride;
(z) pyromellitic anhydride.

EXAMPLE 27

EXAMPLE 1 is modified wherein the modified solid phenolic resin is mixed with blowing agent in an amount up to 50% by weight of the resin while in a closed system under pressure. Then the mixture is released from the closed system and allowed to expand and cool, thereby producing a rigid cellular phenolic resin product.

- (a) compressed air;
(b) nitrogen;
(c) helium, e.g., trichlorofluoromethane;
(d) propane;
(e) methane;
(f) acetylene;
(g) carbon dioxide;
(h) acetone;
(i) acetone;
(j) acetone;
(k) acetone;
(l) acetone;
(m) acetone;
(n) acetone;
(o) acetone;
(p) acetone;
(q) acetone;
(r) acetone;
(s) acetone;
(t) acetone;
(u) acetone;
(v) acetone;
(w) acetone;
(x) acetone;
(y) acetone;
(z) acetone.

- (a) isocyanic acid;
(b) acetic acid;
(c) malic acid;
(d) tartaric acid;
(e) succinic acid;
(f) fumaric acid;
(g) maleic acid;
(h) phthalic acid;
(i) isophthalic acid;
(j) terephthalic acid;
(k) trimellitic acid;
(l) pyromellitic acid;
(m) trimellitic anhydride;
(n) pyromellitic anhydride;
(o) trimellitic anhydride;
(p) pyromellitic anhydride;
(q) trimellitic anhydride;
(r) pyromellitic anhydride;
(s) trimellitic anhydride;
(t) pyromellitic anhydride;
(u) trimellitic anhydride;
(v) pyromellitic anhydride;
(w) trimellitic anhydride;
(x) pyromellitic anhydride;
(y) trimellitic anhydride;
(z) pyromellitic anhydride.

EXAMPLE 28

About 100 parts by weight of the powdered phenolic resin produced in EXAMPLE 27 and up to 10 parts by weight of a gas, such as acetylene, are mixed, then placed in a mold and then heated to about 120° C., thereby expanding the phenolic resin into a cellular product.

EXAMPLE 29

Powdered phenolic resin as produced in EXAMPLE 1 is mixed with powdered methylene-bisphenol-diisocyanate in the ratio of 2:1 by weight, then heated to the melting point of the phenolic resin. The mixture is poured into a solid cellular product which may be used for thermal and sound insulation.

Although specific conditions and ingredients have been described in conjunction with the above examples of preferred embodiments, these may be varied and other reagents and additives may be used without substantial modification, with similar results. Other modifications and applications of the invention will occur to those skilled in the art upon reading this disclosure. These are intended to be included within the scope of this invention as defined in the appended claims.

1. The process for the production of phenolic resin by mixing and reacting the following components:

- (A) substituted organic compound which contains a hydroxyl radical or an epoxy radical and the substituent selected from the group consisting of halogens, acid sulfates, nitrate, acid phosphates, borates, formate, acetate, propionate, laurate, oleate, stearate, cerate, acid malonate, acid succinate, acid citrate, and esters thereof, in the amount of 10 to 100 parts by weight;
(B) monofunctional phenol compound in the amount of 10 to 50 parts by weight;
(C) alkali salt-forming compound in the amount of 1 to 50 parts by weight.

2. The product produced by the process of claim 1.
3. The process of claim 1 wherein up to 300% by weight of a modifying compound, based on the weight of Component A of claim 1, is added to the components.
4. The product produced by the process of claim 3.
5. The process of claim 1 wherein up to 10% by weight of an emulsifier, based on the weight of Component A, B and C of claim 1, is added to the components.
6. The process of claim 1 wherein up to 500% by weight of inert filler material, based on the weight of Component A, B and C of claim 1, is added to the components.
7. The process of claim 1 wherein the substituted organic compound of hydroxyl radical has the general formula of:



where R is a carbon atom or an organic group, substituted or unsubstituted;
where X is the same or different organic group or hydrogen and the organic group is selected from the group consisting of CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_6H_5 , C_6H_4 , C_6H_3 , C_6H_2 , C_6H , C_6 , C_5 , C_4 , C_3 , C_2 , C , H , F , Cl , Br , I , O , S , N , P , As , Se , Te , Bi , Po , At , Rn , Ac , Ba , Sr , Ca , Mg , Be , Al , Ga , In , Tl , Pb , Sn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd , Hg , Cu , Ag , Au , Pt , Pd , Ni , Co , Fe , Mn , Zn , Cd

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SELF-WETTING FOAM PRODUCT AND METHOD OF MAKING SAME

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SELF-WETTING FOAM PRODUCT AND

METHOD OF MAKING SAME

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Association Public-Product Laboratories, Inc.

Continuation-in-part of abandoned application Ser. No.

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2

ADDITIONAL BACKGROUND INFORMATION

It has also been found that urea formaldehyde resins can be foamed to contain wetting agents by mixing the wetting agent with the urea formaldehyde resin prior to foaming and by thereafter introducing foaming catalyst to foam the mass.

SUMMARY OF THE INVENTION

This invention provides a foamed phenolic plastic having interconnected cells and containing anionic sulfonate wetting agent distributed through the plastic material of the mass and rendering the mass highly self-wetting when immersed in liquids. According to this invention, the foam can be produced by thoroughly mixing phenolic resin with a small amount of unreacted anionic sulfonate wetting agent and treating the mixture with an inorganic mineral acid as the foaming catalyst, without undue heating or burning of the mixture, to produce the foamed phenolic product which still contains unreacted anionic sulfonate wetting agent. The anionic sulfonate wetting agent can be isolated from the phenolic and/or acid catalyst during foaming.

In a preferred method, the anionic wetting agent and sulfonate wetting agent are added to two portions. Accordingly, one portion of the anionic wetting agent is added followed immediately by a portion of the sulfonate wetting agent and the liquid is thoroughly mixed; then the remainder of the anionic wetting agent is added followed immediately by the remainder of the sulfonate wetting agent and thoroughly mixed, followed by addition and mixing of the inorganic mineral acid foaming catalyst.

As a preferred feature of this invention, a mass of foam containing carbon black pigment can be converted to a pleasant mossy green color by treatment of the foam with gaseous ammonia. The ammonia also functions to neutralize residual acid catalysts, although preferably it is used only to neutralize to a pH between 6 and 7 since this pH is particularly adaptive to the preservation of flowers.

While this invention is susceptible of embodiment in many different forms, there is shown in the drawings and will be described herein in detail an embodiment of the invention with the understanding that the invention is not considered to be limited by the embodiment illustrated and described.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a section of an embodiment of impregnated phenolic floral foam according to a preferred form of the invention; and

FIG. 2 is a diagrammatic showing enlarged from FIG. 1, of a cell wall for the purpose of showing how the wetting agent can be present within the phenolic foam structure.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring first to the drawings, FIG. 1 illustrates a block 14 of floral foam material having passageway 16 provided therein for supporting flower stems as disclosed by my above identified patent. Sulfonate wetting agent, as indicated by the stippling at 18, is uniformly distributed throughout the block 14 of foamed cellular material and occurs at the surface of the cell walls and may occur even within the cell walls. The cells of block 14 are of the interconnected type providing flow passages from one cell to the next. As seen in FIG. 2, it is believed that the cell walls 20 of the cells in the foamed cellular structure 14 contain, interiorly and exteriorly, sulfonate wetting agent as indicated diagrammatically at 24 within or between protective material

ABSTRACT OF THE DISCLOSURE

Solid self-wetting foam containing ammonium neutralized residue of mineral acid catalyst with interconnected cells having coarsely and generally uniformly distributed unreacted anionic sulfonate wetting agent content of 1% to 3 weight percent isolated by anionic wetting agent from the catalyst residue and the phenolic of the foam, manufactured by mixing phenolic resin and carbon black with anionic wetting agent, mixing in the sulfonate, adding and mixing more anionic wetting agent, foaming the mixture with mineral acid, recovering the resulting solid foam product, and neutralizing residual acid with ammonia to turn the foam from black to green.

The anionic wetting agent and sulfonate wetting agent additions can be split into two additions so that a portion of the anionic wetting agent is added followed by a portion of the sulfonate, the remainder of the anionic wetting agent and then the remainder of the sulfonate. This achieves faster wetting and maximum water absorption in the foam product.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my application Ser. No. 652,225, entitled "Floral Foam and Method of Making Same," filed July 10, 1967, now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

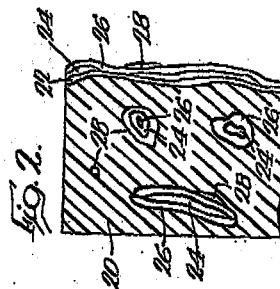
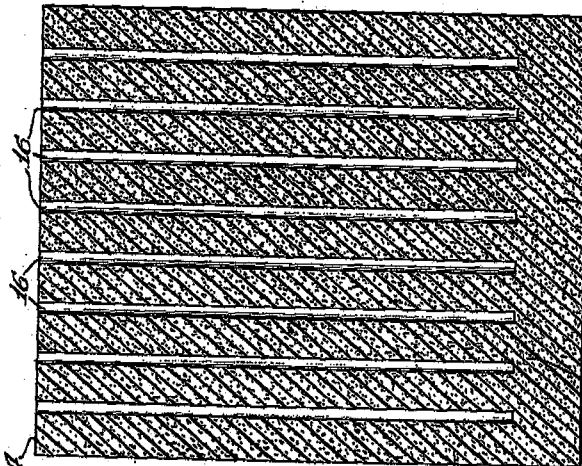
This invention relates to self-wetting, phenolic foams and to a method of making such foams. More particularly, the invention relates to self-wetting phenolic foam masses containing an effective surface active wetting agent rendering the foam capable of rapidly absorbing liquids.

(2) Description of the prior art

My U.S. Pat. No. 3,049,444 describes a self-wetting cellular synthetic plastic material which is impregnated with a wetting agent to improve its self-wetting properties for use as a floral foam. According to that patent, the plastic material is foamed and is then provided with passages for holding flower stems. This wetting agent is applied from the passages to impregnate the interior portion of the foam body.

A search of the prior art since the development of my present invention has revealed that surface active surfactants have been included in phenolic materials during foaming as foam increasing agents in the production of cellular expanded thermoset resins having excellent buoyancy properties by virtue of use of the surface active agents and a peroxide foaming catalyst. The production of such a material is disclosed by Sterling in U.S. Pat. No. 2,629,698. Such foaming can also be conducted using a combination of urea compound and diisocyanate as a foaming catalyst; see Sterling in U.S. 2,608,536.

WETTING AGENT
FOAMED CELLULAR
SYNTHETIC MATERIAL



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4

of mixing time can be made by those in the art to suit their particular desires.

Next, 5 parts by weight of Benzene 2A-1 (solubility 45% active content, diisobutyl 4-decylated oxyphenylene sulfone and 55% water) was added and blended in the mixer for five minutes. As in the case of the Tween 40, the mixing time can be adjusted by those in the art. The Benzene 2A-1 type of sulfonated product is preferred as a wetting agent because it is extremely stable in the presence of both salt and alkali, and is to be added as the foaming catalyst and is later to be neutralized with sodium.

About 8 parts by weight of aged BRL phenolic resin 2739 (a resin-phenolic resin), containing carbon black as a pigment, and another 8 parts by weight of fresh BRL phenolic resin 2739 were blended into the mixture along with 6.6 parts by weight isopropyl ether and 1.8 additional parts by weight Tween 40 and mixing was carried out for about 15 to 30 minutes. It is preferred to include some partly aged resin in the mix to provide better foaming to a desired density by slowing down the curing reaction and thereby eliminating large pressure cracks in the material. After thoroughly mixing, 8 parts by weight of hydrochloric acid was added to the batch, followed by mixing for a short period of time, e.g., one minute. The mixture was then dumped in a mold.

The foamed product recovered from the mold was cut into slabs and placed in a steam-heated chamber and heated to drive off most of the acid catalyst. The heat in the chamber was cut off and small amounts of tin-plate were introduced into the chamber for a period of about one hour. The ammonia gas readily permeated the foam because of the partial vacuum created by previous cooling of the foam from elevated temperatures and the ammonia gas penetrates further into the foam as the foam cools further. The amount of ammonia gas entering the foam is not sufficient to react with or characterize the resin. Benzene 2A-1, the foam after which the cut and black in color due to the presence of the black dye, color material, but the ammonia converts the black color to a very uniform green color which is an attractive color for the foam.

This foam produced shows very low heat blocks and is not subject to pressure. When placed in water, the blocks absorbed water and sank quickly. However, when subjected to a considerable amount of time, the foam floats for a considerable period of time. As an example of the especially preferred method, when I add the wetting time and maximum water absorption in the foam product the above typical example was repeated from the addition and mixing of the foam. Then the 1.5 parts by weight of the Tween No. 40 was added, followed immediately by 2.5 parts by weight of Benzene 2A-1. The light was thoroughly mixed for several minutes and another 1.5 parts by weight of Tween No. 40 was added, again followed immediately by another 2.5 parts by weight Benzene 2A-1. The mixing was continued and then the aged BRL phenolic resin 2739, carbon black, additional fresh BRL phenolic resin 2739, isopropyl ether, additional Tween 40, and hydrochloric acid catalyst were added in as in the typical example. The foam product had a much faster wetting time and higher water absorption properties than the one prepared above.

All parts and percentages given herein are by weight unless otherwise indicated.

1 claim.

1. A method of producing a water absorbing hydrophobic foam of the type useful for foam display, and the like, which method comprises thoroughly mixing a liquid phenol-aldehyde resin with a small amount in the range of 1 to 5 percent by weight of unreacted sulfonate wetting agent while physically isolating the resin from the sulfonate with an addition of a monomeric

6

wetting agent to prevent reaction of the sulfonate with the resin and treating the mixture of phenol-aldehyde resin and unreacted wetting agent with an inorganic mineral acid in the absence of material boiling and pouring of the mixture until the mixture has been foamed and solidified by curing and recovering the resulting foamed phenolic solidified product containing sulfonate wetting agent unreacted with the phenol-aldehyde resin and mineral acid.

2. The method of claim 1 wherein said mineral acid is selected from the class consisting of hydrochloric acid, sulfuric acid and phosphoric acid.

3. The method of claim 1 wherein said amount of sulfonate wetting agent is in the range of 1/4 to 3 percent by weight.

4. The method of claim 1 wherein said sulfonate wetting agent is diisobutyl 4-decylated oxyphenylene sulfone.

5. The method of claim 1 wherein said sulfonate wetting agent is sodium decyl sulfonate.

6. The method of claim 1 wherein the addition of sulfonate wetting agent is prior to adding and mixing the sulfonate wetting agent and in an amount sufficient to physically separate the phenol-aldehyde resin from the later added sulfonate wetting agent.

7. The method of claim 1 including the step of adding additional sulfonate wetting agent after addition of the sulfonate wetting agent and before addition of the mineral acid to an amount physically separating said sulfonate wetting agent from the later added mineral acid.

8. The method of claim 1 wherein said resin contains carbon black pigment and including after foaming the step of treating the foam with ammonia to convert the color to green.

9. The method of claim 1 wherein the addition of a first portion of the monomeric wetting agent is prior to the addition and mixing of a portion of the sulfonate wetting agent and the addition of a second portion of the monomeric wetting agent is prior to the addition of the remainder of the sulfonate wetting agent.

10. The method of claim 9 wherein each addition of a portion of the monomeric wetting agent is followed immediately by addition of sulfonate wetting agent and thorough mixing.

11. The method of claim 10 wherein the two additions of monomeric wetting agent and sulfonate wetting agent are each approximately half of the total amounts of monomeric wetting agent and sulfonate wetting agent, respectively.

12. A method of producing green phenolic foam, which method comprises foaming and curing a mixture of phenol-aldehyde resin, carbon black, and sulfonate wetting agent while physically isolating the resin from the sulfonate with an addition of a monomeric wetting agent to prevent reaction of the sulfonate with the resin and treating the resulting solid foam with ammonia gas until green throughout.

13. A mass of water absorbent cellular plastic comprising foamed and solidified phenol-aldehyde resin containing interconnected cells containing at the cell walls throughout the mass unreacted sulfonate wetting agent.

physically isolated by a monomeric wetting agent rendering the mass highly hydrophilic and quickly wet by aqueous media.

14. The mass of claim 13 wherein said sulfonate wetting agent is present in an amount in the range of 1/4 to 3 percent based on weight of said mass.

15. The mass of claim 13 wherein said sulfonate is reactive toward said mineral acid and including a further means isolating said wetting agent from said acid.

16. The mass of claim 15 wherein said further means is monomeric wetting agent.

17. The mass of claim 13 including unreacted mineral acid within the foamed plastic.

18. The mass of claim 17 wherein said wetting agent is reactive toward said mineral acid and including a further means isolating said wetting agent from said acid.

19. The mass of claim 18 wherein said further means is monomeric wetting agent.

20. The mass of claim 13 wherein said foamed plastic has a structure of unreacted phenolic cell walls defined by foaming with mineral acid catalyst and wherein said sulfonate wetting agent is sandwiched between barrier layers preventing reaction of the wetting agent with the phenolic plastic and acid.

21. The method of claim 1 wherein the addition of monomeric wetting agent is mixed with the phenol-aldehyde resin before said mixing step and including the step after said mixing step and before said treating step of adding and mixing an additional amount of monomeric wetting agent for isolating the sulfonate between the additions of monomeric wetting agent to envelop the sulfonate wetting agent and render it non-reactive to the phenol-aldehyde resin and the mineral acid.

22. A method of producing a phenolic foam wherein a liquid phenol-aldehyde resin is cured by foaming and solidifying using an inorganic mineral acid as the curing agent, the improvement by which the foam is rendered water absorbing and useful for foam display and the like, which improvement comprises incorporating from about 0.1 to about 5 percent by weight of an sulfonate wetting agent in the phenol-aldehyde resin before curing and physically isolating the sulfonate wetting agent from the resin during the curing reaction without the reaction proceeds without material burning of the foam.

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42