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(12) (19) (CA) **Demande-Application**

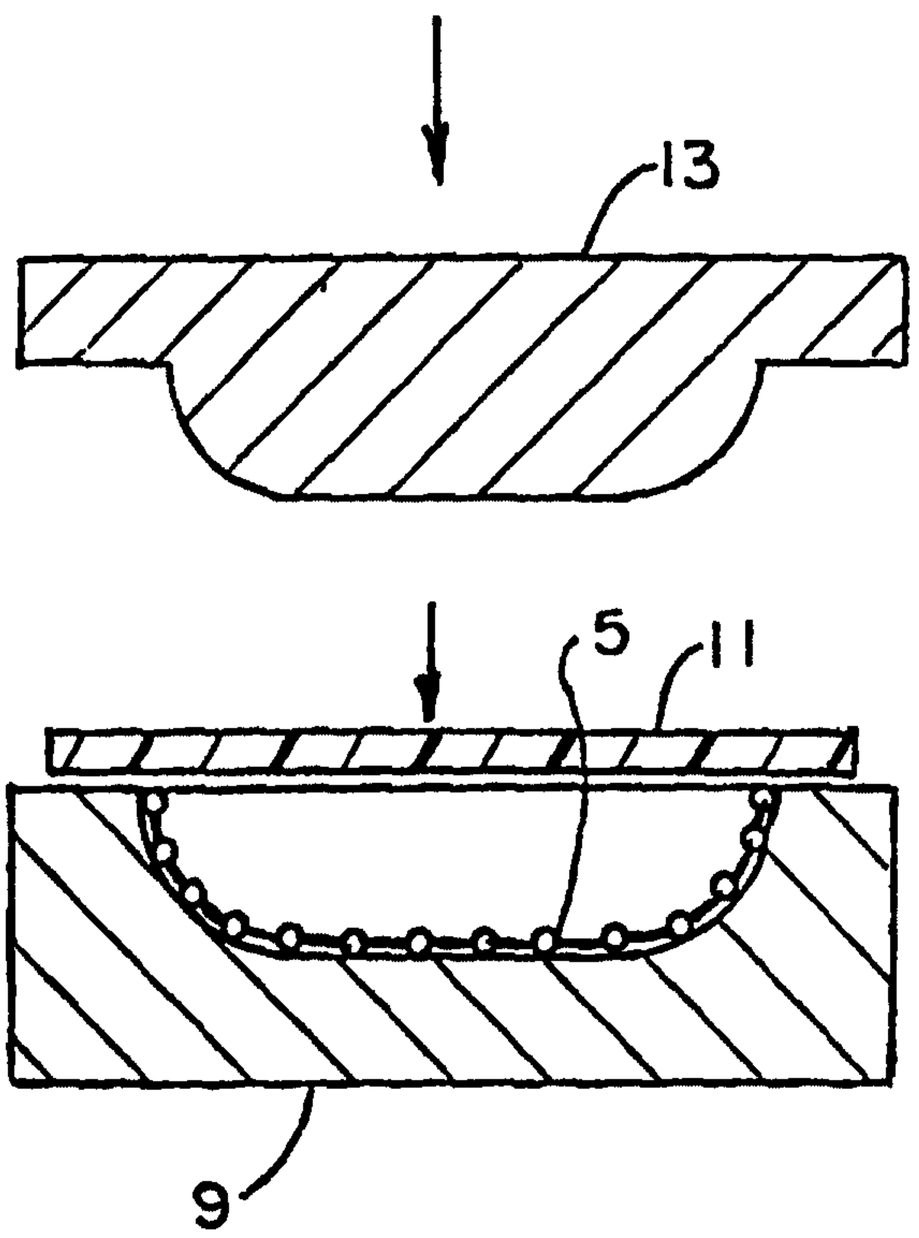
(21) (A1) **2,294,738**
(86) 1998/07/16
(87) 1999/01/28

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(51) Int.Cl.[7] C03C 25/68, B65D 1/40, C03C 25/40, B29C 70/22, B60K 15/03
(30) 1997/07/17 (08/895,918) US

(54) **PROCEDES DE PRODUCTION D'UNE FIBRE DE VERRE ET DE STRUCTURES DE PROTECTION THERMIQUE RESISTANT AUX HAUTES TEMPERATURES**

(54) **METHODS OF MAKING HIGH-TEMPERATURE GLASS FIBER AND THERMAL PROTECTIVE STRUCTURES**



(57) L'invention concerne une fibre de verre capable de résister à des températures supérieures à 1900 °F (1038 °C), produite par traitement d'une fibre de verre, formée de préférence de verre E. On attaque d'abord la fibre de verre avec des acides sélectionnés, puis on traite la fibre attaquée avec des matériaux organo-métalliques

(57) A glass fiber capable of withstanding temperatures in excess of 1900 °F (1038 °C) is produced by treating a glass, preferably E-glass, fiber. The glass fiber is first leached with selected acids, and then the leached fiber is treated with organo-metallic materials of low viscosity, such as a dispersion of low molecular weight water-in-oil

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de faible viscosité, comme par exemple une dispersion d'une émulsion inverse de diméthylpolysiloxane de faible poids moléculaire. On utilise cette fibre pour des applications comprenant l'inclusion de la fibre dans un matériau de revêtement actif résistant au feu ou son inclusion dans une surface de plastique polyoléfinique composite comme par exemple une feuille de polypropylène. La fibre de verre traitée peut être utilisée comme composant isolé ou combinée à un matériau résistant au feu ou ignifuge afin d'accroître les propriétés de résistance au feu de ce dernier. On produit d'autres matériaux composites résistant au feu en pré-enduisant un tissu (1) avec un matériau (3) actif (intumescent ou sublimant), puis en incorporant ce tissu (5) pré-enduit dans une surface de substrat (11) en forme de feuille, de préférence thermoplastique. Le tissu pré-enduit est de préférence collé ou incorporé dans la surface du substrat au cours d'un processus de moulage destiné à donner une forme au composite, pour produire par exemple un conteneur pour automobile de type réservoir de carburant ou base de coffre. Des composites (21) encore différents sont réalisés par collage d'une structure (28) de protection thermique comprenant un tissu (29) pré-enduit d'une composition (31) de protection thermique active, sur une structure (23, 25, 27, 33) formée de fibres revêtues d'un adhésif.

emulsion of dimethyl polysiloxane. The fiber is used in such applications as embedding it in a fire-resistant active coating material or embedding it into one surface of a polyolefin or composite plastic, such as a polypropylene sheet. The treated fiberglass can be used as a sole component or in concert with a fire-resistant or fire retardant material to further enhance its fire-resistant properties. Other fire-resistant composite materials are formed by precoating a fabric (1) with an active (intumescent or subliming) material (3), then embedding the precoated fabric (5) into a surface of a preferably thermoplastic sheet substrate (11). The precoated fabric is preferably adhered to or embedded in the surface of the substrate simultaneously with a molding process which forms the composite into a shape such as an automotive container like a fuel tank or trunk base. Other composites (21) are formed by adhering thermal protective structure (28) comprising a fabric (29) precoated with an active thermal protective composition (31) to a structure (23, 25, 27, 33) formed from fibers coated with an adhesive.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) **International Patent Classification** 6 : **C03C 25/06, B60K 15/03, B65D 1/00, 6/34**

A1

(11) **International Publication Number:** **WO 99/03792**

(43) **International Publication Date:** 28 January 1999 (28.01.99)

(21) **International Application Number:** PCT/US98/14775

(22) **International Filing Date:** 16 July 1998 (16.07.98)

(30) **Priority Data:**

08/895,918	17 July 1997 (17.07.97)	US

(63) **Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application**

US	08/895,918 (CIP)
Filed on	17 July 1997 (17.07.97)

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(81) **Designated States:** AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

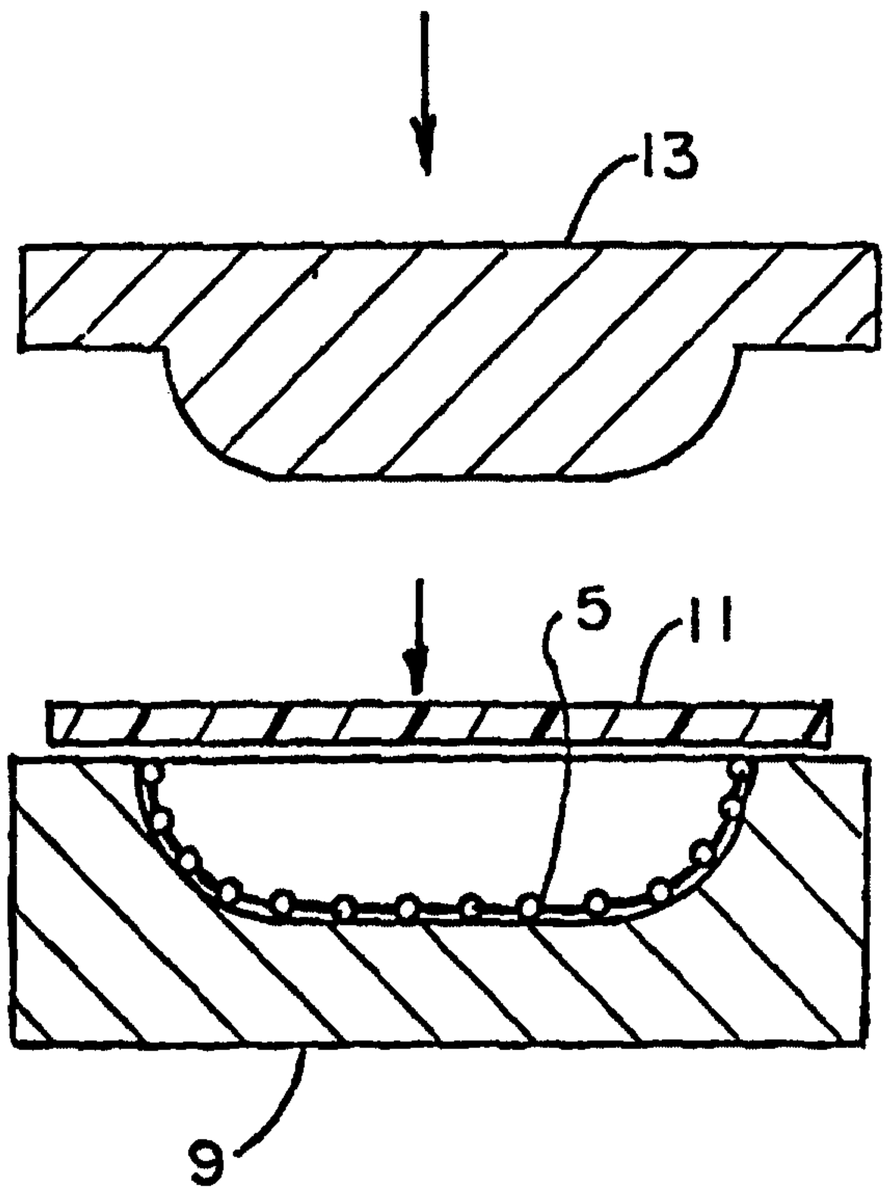
Published

With international search report.

(54) **Title:** METHODS OF MAKING HIGH–TEMPERATURE GLASS FIBER AND THERMAL PROTECTIVE STRUCTURES

(57) **Abstract**

A glass fiber capable of withstanding temperatures in excess of 1900 °F (1038 °C) is produced by treating a glass, preferably E–glass, fiber. The glass fiber is first leached with selected acids, and then the leached fiber is treated with organo–metallic materials of low viscosity, such as a dispersion of low molecular weight water–in–oil emulsion of dimethyl polysiloxane. The fiber is used in such applications as embedding it in a fire–resistant active coating material or embedding it into one surface of a polyolefin or composite plastic, such as a polypropylene sheet. The treated fiberglass can be used as a sole component or in concert with a fire–resistant or fire retardant material to further enhance its fire–resistant properties. Other fire–resistant composite materials are formed by precoating a fabric (1) with an active (intumescent or subliming) material (3), then embedding the precoated fabric (5) into a surface of a preferably thermoplastic sheet substrate (11). The precoated fabric is preferably adhered to or embedded in the surface of the substrate simultaneously with a molding process which forms the composite into a shape such as an automotive container like a fuel tank or trunk base. Other composites (21) are formed by adhering thermal protective structure (28) comprising a fabric (29) precoated with an active thermal protective composition (31) to a structure (23, 25, 27, 33) formed from fibers coated with an adhesive.



METHODS OF MAKING HIGH-TEMPERATURE GLASS FIBER AND THERMAL PROTECTIVE STRUCTURES

Technical Field

This invention relates to a glass form, preferably a fiber, which resists high temperatures, at least 1900° F. (1038° C.) and higher, while retaining at least some of its tensile strength and other physical properties. It also relates to structures, including automotive structures, which can resist high temperature for a predetermined time.

Background Art

In numerous applications, fabrics are utilized in systems which resist high temperatures. An example of the use of such fabrics is in reinforced coating systems. In these systems, the fabric is embedded in a char-forming, fire-resistive coating such as those described in Deogon, U.S. Patent No. 5,591,791. Briefly, such coatings include ablative coatings, which swell to less than twice their original thickness when exposed to fire or other thermal extremes, intumescent coatings such as those disclosed in Nielsen et al., U.S. Patent 2,680,077, Kaplan, U.S. Patent 3,284,216, Ward et al., U.S. Patent 4,529,467, or Deogon, U.S. Patent No. 5,591,791, which swell to produce a char more than five times the original thickness of the coating, and subliming char-forming coatings of the type disclosed in Feldman, U.S. Patent 3,849,178, which undergo an endothermic phase change and expand two to five times their original thickness to form a continuous porosity matrix. The intumescent and subliming coatings are denoted "active" thermal protective coatings.

The time required for a given temperature rise across a predetermined thickness of the composition, under specified heat flux, environmental, and temperature conditions, is a measure of the composition's effectiveness in providing thermal protection to an underlying substrate.

Eventually, the char is consumed by physical erosion and by chemical processes, such as oxidation by oxygen in the air and by free radicals produced by the coating or otherwise in a fire environment, and protection is substantially

reduced. Before the char is totally consumed, degradation of the char layer leaves it crumbled and without the necessary strength to sustain itself, causing it to fail by being blown off or simply falling off (spalling).

Some of these chars degrade rapidly during exposure to high temperature, high heat flux environments. In the case of coatings which swell when exposed to thermal extremes, the degradations are usually in the form of fissures which are formed in the char as a result of differential thermal stresses produced by the high thermal gradients within the char, and differential thermal expansion between the virgin material and the char.

To increase the strength of char layers during exposure to thermal extremes, and to limit spalling and fissures, fabrics have long been incorporated in the coating materials. As set out in Feldman et al., U.S. Patent No. 5,622,774, fiberglass fabric provides an inexpensive, easy to install, reinforcement in many high temperature applications. In certain applications, however, such as coatings which may be exposed to high velocity petroleum fires or to high-temperature, high heat flux fires which will raise the fabric to temperatures above the softening point of the glass (around 1600° F., 871° C.), the fiberglass fabric has disintegrated. Other fabrics have therefore been required. Graphite cloth, as taught in the foregoing Feldman et al. U.S. Patent 5,622,774 and in Kobayashi et al., U.S. Patent No. 5,401,793, is very expensive. Refractory materials, such as quartz (Refrasil) fabric is also expensive. Metal mesh is inexpensive but it is heavy and difficult to install, particularly because it generally requires welding metal studs to the substrate to be protected.

Other examples of fabric-reinforced systems are laminates in which the fabric is embedded directly in a structural resin material itself, for example in the structure of a furnace or a rocket nozzle. Generally, these materials also produce a char when exposed to sufficiently high temperatures, although in many applications they are routinely exposed to high temperatures below their char-forming temperature for extended periods. In other applications they are exposed for short periods to temperature, heat flux, and environmental

conditions which do not cause a char to form, but which are sufficiently high to cause serious loss of structural properties. Examples of these latter systems are automobile gasoline tanks and trunks, which can be made of plastic material (generally a thermoplastic material) if they can pass a test involving preventing structural failure (such as drop through in the case of a trunk or an explosion in the case of a gasoline tank) when the trunk or tank is placed over a fire of a specified temperature and intensity for a predetermined period such as two minutes. Also, other automotive components, such as trunk liners, parcel shelves, and interior door panels, are sometimes formed of felted natural or synthetic fibers having a thermoplastic binder or substrate. In all of these conditions, a fabric which resists complete degradation under the foregoing conditions can provide sufficient structural integrity to impede failure of the system. Other approaches to providing sufficient integrity to thermoplastic automotive components and other automotive components containing thermoplastic binders are also needed.

Attempts have been made for many years to produce a glass fiber which retains a substantial portion of its mechanical properties even when subjected to very high temperatures, greater than 1600° F. (871°C.), and preferably on the order of 1900° to 2000° F. (1038° to 1093° C.). Examples are Nordberg, U.S. Patent No. 2,461,841, Parker et al., U.S. Patent No. 2,491,761, and Leeg et al., U.S. Patent No. 2,992,960. These patents all involve leaching of the glass fiber with mineral acid, followed by treatment with a sizing material. Heretofore, such attempts have failed to provide a reliable, reproducible, and efficient process of converting commercial grade fiberglass (such as Type E and Type F glass fibers) into a material capable of withstanding elevated temperatures and aerodynamic shear which may be coupled with elevated temperatures.

Likewise, no economical, simple means is known for protecting thermoplastic and thermoplastic-containing structures, such as automotive components from high temperatures.

Summary of Invention

In accordance with one aspect of the present invention, generally stated, a method of making a heat-resistant fiberglass fabric is provided comprising soaking a fiberglass fabric in a carefully selected acid bath for a selected time at a selected temperature. We have found that soaking the fiberglass in a mixture of acids containing at least 15% sulfuric acid at room temperature for a period of more than twenty-four hours, preferably at least about forty-eight hours, produces a material which maintains a substantial part of its physical characteristics even when heated to a temperature of at least 1600° F. (871° C.) for a period of at least one hour. The molality of the mixed acids is below 8, preferably around 5. It is anticipated that shorter soak times may be achieved with higher temperatures.

We have also found that the acid-treated fiberglass can be given superior qualities, such as improved "hand" (texture) both before and during exposure to high temperatures, by soaking the fiberglass in a low viscosity organo-metallic material, such as a low molecular weight silicone to fill the pores of the glass. The silicone is preferably in the form of a water-in-oil emulsion of low molecular weight silicone, such as dimethyl polysiloxane. The use of a water-in-oil emulsion, rather than an oil-in-water emulsion, inhibits the formation of silicone micelles and enhances absorption of the silicone into the pores of the glass fibers. We have found that soaking a fiberglass fabric for a period of more than forty-eight hours, preferably at least seventy-two hours, at room temperature in a low molecular weight, low viscosity, silicone bath produces superior results.

Certain combinations of acid treatment and treatment with low molecular weight silicone have been found to produce materials which consistently will withstand being heated to a temperature of 1900° F. (1038° C.) for at least one hour in a muffle furnace.

The improved fabric has numerous uses, as will be apparent to those skilled in the art. It provides a superior reinforcement in thermal protective coating systems of the types previously described. For example, it may be

embedded in fire-protective coatings of subliming, intumescing and ablative types, and has been found to provide excellent results as a reinforcement in sprayed-on subliming coating systems. It may also be used in active or passive cast or molded self-supporting thermal protective systems such as the system described in Feldman, U.S. Patent No. 4,493,945.

In accordance with another aspect of the invention, structural members formed of thermoplastic resins are strengthened and protected from fire for extended periods by incorporating in them a high-temperature fiberglass fabric made in accordance with the present invention. The fabric is preferably pressed into a resin sheet as the sheet is formed into a container or other functional entity.

In accordance with a another aspect of the present invention, generally stated, members formed at least in part of thermoplastic resins are strengthened and protected from fire or other hyperthermal conditions for extended periods by incorporating in them a fabric or mesh which is pretreated with an active (intumescing or subliming) thermal protective coating material and then embedded in the thermoplastic material. The fabric is preferably a high-temperature fiberglass made by the method of the aforementioned parent application, although other fabrics including ordinary fiberglass, other inorganic materials, synthetic polymeric materials and natural organic materials such as cotton may also be used. Preferably, the fabric comprises an open weave mesh having from 0.5 to 30 openings per square centimeter. The active fire retardant material can be impregnated into the fabric material or surface coated on the fabric. Preferably, a coating of from 100 to 1,000 grams per square meter is applied. It can be completely cured in a rigid or elastic form; it can also be supplied in a precured condition or in a semi-cured condition to be cured during processing. The cells of the treated or impregnated fiberglass can be preferably open or may be filled. For some materials such as polypropylene, an open cell is preferred as it enables the softened polypropylene to pass through the opening and form a mechanical lock. The pretreated fabric is preferably embedded in or

bonded to a surface of the substrate, generally the surface which is expected to be exposed directly to a flame or other hyperthermal condition.

In accordance with a method of the invention, a composite structure is formed by pretreating a fabric with an active thermal protective material, placing the pretreated fabric in a mold, and bonding the pretreated fabric to a substrate while the substrate is being formed in the mold. In a preferred embodiment, the substrate is formed at least partly of a thermoplastic resin such as a polyolefin which is heated to a softening temperature and which adheres chemically and mechanically to the pretreated fabric in the mold during its molding process.

Brief Description of Drawing

FIG. 1 is a fragmentary top plan view of a thermal protective structure for use in practicing certain aspects of the present invention.

FIG. 2 is a view in side elevation thereof.

FIG. 3 is a somewhat diagrammatic sectional view showing a step in molding a composite container incorporating the structure of FIGS. 1 and 2 in accordance with one aspect of the present invention.

FIG. 4 is a somewhat diagrammatic sectional view, corresponding to FIG. 3, showing another step in the process.

FIG. 5 is a somewhat diagrammatic sectional view of the composite container formed in the process of FIGS. 3-4.

FIG. 6 is an exploded view showing the layers of a composite formed in accordance with another aspect of the present invention.

Best Modes for Carrying Out the Invention

To determine the effect of different acid compositions and exposure times at a constant temperature and acid molality, and to determine the effect of further treatment in a low molecular weight polysiloxane at a constant temperature for different time periods, a series of tests was made. The results of these tests are shown in Table 1.

Table 1

Sample	Acid Bath Mole Ratio	Time in Bath	Wt Change	Time in Silicone	Wt Change		Wt Change		Comments
No.	Cl NO_3 SO_4	Hr.	%	Hr.	From orig	From acid	In muffle	From orig.	
Blank							-12.44%	-12.44%	shrunk, melted
A-1	1 1 1	3	-0.08%	0	-0.08%	0.00%	-11.76%	-11.83%	fragile, crisp
A-2	1 1 1	3	-0.77%	6	5.82%	6.64%	-16.89%	-12.05%	slightly fragile
A-3	1 1 1	3	-0.34%	24	6.28%	6.63%	-17.40%	-12.22%	slightly fragile
A-4	1 1 1	3	0.00%	72	7.68%	7.68%	-17.38%	-11.04%	slightly fragile
A-5	1 1 1	8	-0.30%	0	-0.22%	0.08%	-13.80%	-13.98%	less fragile
A-6	1 1 1	8	-0.69%	6	5.66%	6.39%	-17.24%	-12.55%	less fragile
A-7	1 1 1	8	-0.35%	24	7.51%	7.89%	-18.56%	-12.44%	less fragile
A-8	1 1 1	8	-0.60%	72	7.01%	7.64%	-17.37%	-11.58%	very nice
A-9	1 1 1	24	-2.92%	0	-2.93%	-0.10%	-17.81%	-20.21%	less fragile
A-10	1 1 1	24	-3.88%	6	2.84%	6.83%	-21.10%	-18.86%	less fragile
A-11	1 1 1	24	-1.92%	24	6.92%	8.97%	-20.33%	-14.81%	less fragile
A-12	1 1 1	24	-2.12%	72	0.18%	2.30%	-20.07%	-19.92%	nice
A-13	1 1 1	48	-6.59%	0	-6.15%	0.04%	-23.14%	-27.86%	very nice - fuzzy
A-14	1 1 1	48	-7.04%	6	3.91%	11.22%	-26.89%	-24.03%	soft - fuzzy
A-15	1 1 1	48	-6.38%	24	3.98%	10.62%	-26.33%	-23.39%	very nice - fuzzy
A-16	1 1 1	48	-4.54%	72	-3.38%	1.00%	-26.16%	-28.66%	very nice - fuzzy
B-1	2 3 1	3	-0.25%	0	-0.27%	-0.02%	-10.58%	-10.82%	fragile
B-2	2 3 1	3	-0.39%	6	6.86%	7.28%	-14.91%	- 9.07%	fragile
B-3	2 3 1	3	0.02%	24	6.01%	5.98%	-18.29%	-13.38%	fragile
B-4	2 3 1	3	-0.32%	72	7.62%	7.97%	-16.37%	-10.00%	less fragile
B-5	2 3 1	8	-0.85%	0	-0.79%	0.05%	-13.56%	-14.24%	fragile
B-6	2 3 1	8	-0.95%	6	4.26%	5.25%	-17.62%	-14.11%	less fragile
B-7	2 3 1	8	-1.10%	24	5.56%	6.71%	-15.79%	-11.11%	nice
B-8	2 3 1	8	-0.85%	72	5.48%	6.38%	-18.26%	-13.78%	slightly fragile
B-9	2 3 1	24	-5.47%	0	-5.27%	-0.10%	-16.44%	-20.85%	less fragile
B-10	2 3 1	24	-3.24%	6	1.86%	5.16%	-20.06%	-18.56%	nice
B-11	2 3 1	24	-4.40%	24	4.70%	9.31%	-20.89%	-17.18%	less fragile
B-12	2 3 1	24	-4.31%	72	0.79%	5.14%	-20.59%	-19.96%	nice
B-13	2 3 1	48	-10.86%	0	-9.58%	0.23%	-19.86%	-27.54%	very nice-fuzzy
B-14	2 3 1	48	-10.29%	6	1.02%	11.42%	-24.77%	-24.00%	nice - fuzzy
B-15	2 3 1	48	-9.63%	24	3.29%	13.24%	-24.99%	-22.52%	nice - fuzzy
B-16	2 3 1	48	-10.89%	72	-0.31%	10.54%	-24.76%	-24.99%	nice - fuzzy
C-1	4 2 1	3	-0.09%	0	-0.10%	-0.01%	-13.10%	-13.19%	fragile
C-2	4 2 1	3	0.00%	6	5.52%	5.52%	-16.48%	-11.87%	slightly fragile
C-3	4 2 1	3	-0.15%	24	7.62%	7.78%	-16.79%	-10.45%	less fragile

C-4	4 2 1	3	-0.08%	72	7.30%	7.39%	-18.17%	-12.20%	slightly fragile
C-5	4 2 1	8	-0.94%	0	-0.85%	0.07%	-13.07%	-13.81%	slightly fragile
C-6	4 2 1	8	-1.04%	6	4.57%	5.66%	-18.14%	-14.40%	less fragile
C-7	4 2 1	8	-0.67%	24	4.30%	4.99%	-18.83%	-15.34%	slightly fragile
C-8	4 2 1	8	-0.53%	72	4.78%	5.34%	-19.15%	-15.28%	slightly fragile
C-9	4 2 1	24	-4.83%	0	-4.63%	-0.02%	-16.68%	-20.54%	less fragile
C-10	4 2 1	24	-5.38%	6	1.54%	7.00%	-18.95%	-17.70%	slightly fragile
C-11	4 2 1	24	-5.18%	24	3.98%	9.36%	-19.70%	-16.50%	less fragile
C-12	4 2 1	24	-4.62%	72	1.52%	6.21%	-19.55%	-18.32%	less fragile
C-13	4 2 1	48	-11.42%	0	-10.10%	0.17%	-18.76%	-26.96%	nice
C-14	4 2 1	48	-11.08%	6	1.59%	12.85%	-23.59%	-22.38%	less fragile
C-15	4 2 1	48	-10.30%	24	4.90%	15.71%	-25.06%	-21.38%	less fragile
C-16	4 2 1	48	-10.51%	72	0.06%	10.57%	-22.90%	-22.85%	less fragile
D-1	1 1 4	3	8.87%	0	1.78%	-7.24%	-15.64%	-14.14%	slightly fragile
D-2	1 1 4	3	1.56%	6	10.81%	9.08%	-17.73%	-8.84%	slightly fragile
D-3	1 1 4	3	0.88%	24	12.22%	11.23%	-16.50%	-6.30%	fragile
D-4	1 1 4	3	1.29%	72	9.14%	7.73%	-20.98%	-13.76%	fragile
D-5	1 1 4	8	1.32%	0	1.36%	0.02%	-15.18%	-14.03%	nice
D-6	1 1 4	8	0.77%	6	9.52%	8.67%	-21.82%	-14.38%	slightly fragile
D-7	1 1 4	8	0.27%	24	7.21%	6.93%	-19.01%	-13.17%	slightly fragile
D-8	1 1 4	8	0.58%	72	4.50%	3.90%	-19.29%	-15.66%	less fragile
D-9	1 1 4	24	1.45%	0	1.71%	0.24%	-18.33%	-16.93%	nice
D-10	1 1 4	24	0.63%	6	12.25%	11.54%	-22.71%	-13.25%	nice fuzzy
D-11	1 1 4	24	2.10%	24	12.89%	10.52%	-22.24%	-12.21%	nice fuzzy
D-12	1 1 4	24	2.09%	72	0.08%	-2.01%	-21.21%	-21.15%	nice
D-13	1 1 4	48	4.73%	0	8.04%	2.93%	-23.89%	-17.77%	nice
D-14	1 1 4	48	10.98%	6	18.84%	5.78%	-24.70%	-10.52%	soft fuzzy
D-15	1 1 4	48	10.92%	24	22.15%	8.80%	-24.48%	-7.75%	nice fuzzy
D-16	1 1 4	48	11.01%	72	-1.13%	-12.01%	-23.98%	-24.84%	nice fuzzy
E-1	1 0 4	3	0.29%	0	0.31%	0.02%	-11.51%	-11.23%	slightly fragile
E-2	1 0 4	3	0.54%	6	10.84%	10.25%	-18.64%	--9.82%	slightly fragile
E-3	1 0 4	3	0.46%	24	12.85%	12.33%	-18.33%	-7.84%	slightly fragile
E-4	1 0 4	3	0.56%	72	9.88%	9.27%	-21.75%	-14.02%	less fragile
E-5	1 0 4	8	2.41%	0	2.55%	0.08%	-17.69%	-15.60%	slightly fragile
E-6	1 0 4	8	2.64%	6	11.64%	8.70%	-18.82%	-9.37%	slightly fragile
E-7	1 0 4	8	3.02%	24	8.06%	4,80%	-18.54%	-11.97%	less fragile
E-8	1 0 4	8	3.49%	72	3.58%	-0.03%	-18.44%	-15.52%	slightly fragile
E-9	1 0 4	24	7.70%	0	8.08%	-0.24%	-22.04%	-15.74%	very nice
E-10	1 0 4	24	5.88%	6	14.80%	8.05%	-24.62%	-13.47%	soft fuzzy
E-11	1 0 4	24	7.78%	24	17.76%	9.78%	-24.16%	-10.69%	very nice

E-12	1 0 4	24	7.04%	72	-0.18%	-7.21%	-21.80%	-21.94%	nice fuzzy
E-13	1 0 4	48	10.58%	0	11.47%	-0.32%	-22.83%	-13.98%	soft fuzzy
E-14	1 0 4	48	8.31%	6	18.63%	8.78%	-25.45%	-11.56%	very nice fuzzy
E-15	1 0 4	48	11.11%	24	15.43%	2.62%	-25.56%	-14.07%	nice fuzzy
E-16	1 0 4	48	3.15%	72	0.37%	-2.79%	-24.33%	-24.05%	nice fuzzy
	Examined E13, A15, B15, C15, D15 & E15								
	E13 & E15 showed no visible differences under 30x microscope								
	Weave threads of samples E13, E15 & D15 looked swollen								
	These samples also had a softer "hand" and drooped more.								

In making these tests, the following procedure was followed.

An acid bath was prepared by weighing the relative quantities of acid, mixing the acid thoroughly, and adding sufficient water to obtain a 5.0 molal solution. The selection of the 5.0 concentration was arbitrary, but it has been found that molalities of 8 or above do not function as well.

Samples of the unraveled fiberglass material (Type E, J.P. Stevens Type 1353) were weighed and then totally immersed in the acid bath for the indicated number of hours.

At the completion of each individual immersion period, the fiberglass sample was removed from the acid bath, carefully washed with clean water, dried, and weighed. This weight was compared to the weight of the sample in its virgin state.

Some of the acid-treated fiberglass samples were then totally immersed in a bath of low molecular weight dimethyl polysiloxane in the form of a dispersion of water in the polysiloxane oil. The dispersion was formed from a concentrate of low molecular weight dimethyl polysiloxane in a water-in-oil emulsion, as sold by Blackhawk Specialty Products, Inc., Rock Island, Illinois, as its BSP-89W. The time spent in the silicone bath is recorded in Table 1 for each sample.

The sample was then placed in a muffle furnace which was maintained at a constant temperature of about 1600° F.(871° C.). This temperature was selected to represent a typical average temperature within a char layer which results from the exposure of a subliming or intumescing material which is

applied to a steel substrate in thicknesses that are capable of meeting relevant ASTM E-119 type fires for one, two, or more hours in duration.

The sample was kept in this environment for a period of about sixty minutes, then removed from the muffle furnace and cooled. Upon completion of cooling, it was examined for embrittlement, "hand" retention, and weight loss. If the sample retained its "hand" (indicated by the word "nice" in the comments section of Table 1) then it was subjected to further tests. It will be seen from Table 1 that samples A-8, A-12 through A-16, B-7, B-10, B-11 through B-16, C-13, D-5, D-9 through D-16, and E-9 through E-16 met the foregoing criterion and were tested further. All of these samples were soaked in the room temperature acid for a period in excess of three hours. All but C-13 had been soaked in a mixture including in excess of 15% sulfuric acid.

Fresh samples taken from corresponding lots as the foregoing samples were further exposed to 1600° F. (871° C.) in the muffle furnace for a period of sixty minutes. After cooldown, they were again checked for "hand retention," and results recorded. The samples which were embrittled were eliminated from further testing, leaving samples A-13 through A-16, D-13 through D-16, and E-13 through E-16 to be tested further.

Fresh samples taken from corresponding item lots as the foregoing samples were exposed to a muffle furnace fire at a temperature of about 1900° F to about 2000° F (1038°-1093° C.) for a period of one hour. This temperature was selected because it represents a thermal environment most likely encountered within the char layer of a subliming or intumescing material which is exposed to a hydrocarbon fire environment as defined by Underwriters Laboratory procedure 1709 or a jet fire environment as defined by British Offshore Technology Report OTO 93 028 (21 December 1993). After cooldown, the samples were checked for "hand" retention, and results were recorded. The three item samples which were not embrittled were A-16, D-13, and E-16. All the most successful samples had been soaked at room temperature for over twenty-four hours in an acid solution containing in excess

of 15% molal sulfuric acid, and two of the three samples had been soaked at room temperature for over twenty-four hours in the low-viscosity silicone emulsion.

Preliminary fire tests of the treated fiberglass fabric in a subliming fire-protective coating system indicate that the system provides superior results.

To further test the treated fabrics, and to demonstrate their usefulness in composite materials, the material was embedded in small (approximately 10 cm square) test polypropylene sheets as follows. In separate tests, two active fire protective materials were applied to the fabric: a subliming material (Thermal Science, Inc., THERMO-LAG 440-1) and a thin-film subliming and intumescent material (Thermal Science, Inc. THERMO-LAG 2000). Both these materials are flexible epoxy polysulfide based materials containing a subliming agent. They both swell and undergo an endothermic phase change when exposed to hyperthermal conditions. The materials are formulated to provide different amounts of swelling. In each case, the active thermal protective material was thinned in a solvent or low viscosity resin diluent. The treated fiberglass fabric was placed in a container of the thinned material and squeezed in a wringer to remove excess coating. As shown in FIGS. 1 and 2, this produces a fabric 1 coated with material 3 to form a thermal protective structure 5. The coating 3 covers the fibers of the fabric 1 but does not close the individual cells in the fabric mesh, leaving openings 7. The coated fabric was heated to semicure the subliming material or to cure the intumescent material. The fiberglass remained somewhat elastic.

Polypropylene is a hard material with a surface that is difficult to adhere to. As shown in FIGS 3-5, a molding process was utilized to embed the thermal protective structure 5 in a surface of a polypropylene sheet 11. The test square was heated to 200° to 210° C. The female portion 9 of a mold was heated to 60-70° C. The mold includes a ram with a platen 13 which is heated to 60-70° C. The thermoplastic square 11 was quickly placed into the mold with the precoated fabric 5 on top of it, and the ram was be moved quickly to mold the

plastic before a skin is formed on the plastic. The sample was removed from the mold. This process caused the polypropylene to exude through the openings in the woven fabric and physically lock the fabric to the plastic sheet, so that part of the fabric 5 was embedded in the sheet and part remained visible at the surface of the sheet, as shown in FIG. 5. Comparative flame tests without reinforcement, with untreated fiberglass, with treated fiberglass, and with treated fiberglass coated with each of the active thermal protective materials showed that the treated fiberglass systems provided substantial increases in time to failure, and the coated fiberglass provided dramatic increases in time to failure. The thermal protective structure 5 was oriented on the flame side in the tests.

Based on the foregoing tests, it is believed that the treated fiberglass fiber of the present invention can be embedded into thermoplastic structures by the same process of incorporation during the molding process. Other fibers, coated with active thermal protective materials, can also be embedded into thermoplastic structures. Composite sheets including the treated and/or coated fabric may also be formed either by passing a single heated thermoplastic sheet and a sheet of the fabric between heated rollers, or by sandwiching the fabric between sheets of thermoplastic. In other embodiments, the coating of material on the fabric does close the individual cells and creates a continuous sheet of thermally protective structure which is bonded more easily to the surface of a substrate when the thermally protective structure is not embedded in the substrate.

A polypropylene trunk base, for use in holding the spare tire of an automobile at the bottom of an automobile trunk, is one example of a structure formed by the foregoing processes. Such a trunk base can be formed as an open rectangular box by embedding a fabric, including the treated fabric of the present invention or a fabric coated or impregnated with an active thermal protective material, into a polypropylene sheet as the sheet is formed into the trunk base. Alternatively, one or more polypropylene sheets can be formed into

composites before the molding operation. A polypropylene automotive fuel tank may be formed by the same methods, by forming the tank as two open shells and welding the shells together or by blow-molding the tank in a mold which is lined with a fabric that has been treated or precoated with an active thermal protective material.

Likewise, various automotive structures may be formed of felted natural fibers, such as linen fibers, and reinforced by embedding or otherwise securing to a face of the liner a fabric that has been precoated with an active thermal protective material. Such felted natural fiber sheets are preferably formed with an organic polymer adhesive or binder which holds the fibers together and which aids in holding the precoated fabric to the sheet when it is molded. The polymer binder softens at a temperature below the activation temperature of the active thermal protective material. For example, the binder may be activated at a temperature of about 200° C. and the active thermal protective composition may be activated at a temperature of 280°C. to 350°C.

An example of such a structure is a trunk liner. A portion of such a liner is shown in FIG. 6, in exploded form. The liner 21 is formed from two flexible batts 23 and 25 of flax strands coated with a thermally activated binder material with two thin polyethylene layers 27 sandwiched between them. Such trunk liners are known, a commercial version being produced by Thermoplast Company of Idstein, Germany. A decorative carpet 33 is placed on the free side of the batt 25, as is conventional. The composite is then molded and compressed by alternately hot pressing and cold pressing in a mold of suitable dimensions at suitable temperatures for suitable periods of time, as is known in the art. The pressing processes soften the binder and form a thinner, rigid, shell having a thickness of about seven millimeters.

The conventional liner is greatly improved by the use of a thermal protective structure 28 formed of a fiberglass mesh 29 precoated with FIRE-SORB 2001 (Nu-Chem, Inc., Fenton, Missouri, USA) flexible subliming intumescent thermal protective coating 31. The thermal protective structure 28

is formed from ordinary (E-glass) fiberglass coated with 600 to 800 grams per square meter of subliming material, to give a structure 28 about one-half millimeter thick. The coating covers the openings and forms a continuous film in this embodiment. The subliming material is an epoxy polysulfide which contains sublimers and other additives to make it flexible under the conditions of molding. The thermal protective structure 28 is laid over the batt 23. Optionally, a much thinner batt 35 of the flax material and binder is laid over the thermal protective structure 28. The protective structure 28 is laminated to the surface of the batt 23 using eighty bar pressure at a temperature of 220°C. for twenty seconds. When the thinner batt 35 is overlaid on the protective structure 28, the same molding conditions are used. In the molding process, the thermal protective structure 28 becomes adhered to the batt 23. Because the shell will be placed in an automotive trunk with the inner portion of the shell facing in the direction of the fuel tank, the thermal protective structure 28 is on the inside of the shell in this illustrative embodiment.

Tests of the liner structure 21 without the upper layer 35 show greatly lengthened times to failure when exposed to a 1,000°C. fire of controlled intensity. In the optional construction, the precoated mesh is hidden by the thin upper layer of compressed flax; under fire conditions, however, the upper layer quickly burns off and exposes the active thermal protective material. In both cases, the active protective material expands to about eight times its original thickness (eight mm from an initial half mm) while absorbing energy and producing an open cell matrix through which the sublimed gasses transpire, to provide a greatly extended time to failure of the structure. Preliminary tests indicate that a structure without the thermal protective structure 28 will fail under test conditions in less than forty-five seconds, while the protected structure of the present invention suffers little structural damage in over four minutes.

In applications where the structure is a container, the mesh is illustratively a single piece which extends across a lower side of the bottom and

up at least a part of the outside of an upstanding wall of the structure. In any of these cases, the present invention provides greatly extended times to failure in standard tests involving placing the thermoplastic container or other automotive structure over a standard fire and in other standard tests.

As variations within the scope of the appended claims will be apparent to those skilled in the art, the foregoing description is set forth only for illustrative purposes and is not meant to be limiting. For example, other types of fiberglass may be treated in accordance with the invention. Other combinations of acids may by utilized. The acid bath may include additives, such as silicates for example. As previously noted, the time of acid or resin treatment may be reduced if the temperature of the bath is increased. Other silicones and other low viscosity organo-metallic resins than silicones may be utilized in the post-acid bath treatment of the fiberglass. The treated fiberglass may be used in other high-temperature systems. For example, a composite material may be formed of at least one layer of thermoplastic having embedded therein fibers produced by the acid treatment method of the present invention. Also, a thermal protective composition may be produced having dispersed therein fibers produced by the acid treatment method of the present invention. Examples of such thermal protective compositions are a coating applied to a substrate and a preformed self-supporting structure.

The substrates of the composites of the invention may be formed of other polyolefins (such as polyethylene), other thermoplastics and even thermoset resins, and may be reinforced with various fibers. In the case of structures (mats) formed by pressing batts of fibers coated with adhesive binders, the fibers are preferably natural (such as flax, hemp, or cotton), and the adhesive binder is also preferably recyclable. It will be understood that the binder may be activated by water or otherwise, rather than by heat, although heat-activated binders are presently greatly preferred. The substrate of the composite is preferably moldable into a sheet which is many times wider and longer than its thickness, and the fabric is preferably adhered to the substrate

during the molding operation. It will be understood, however, that the composites may be formed by adhering the pretreated fabric to the substrate after the substrate is molded, although such a process is both slower and more complex than molding and adhering or embedding in a single step. The composites may be formed into other structural containers and entirely other structures, such as other automotive elements (like package shelves and door facings), firewalls, and other high temperature barriers such as used on jet engines. The fabric to which the active thermal material is applied before being secured to the substrate is preferably fiberglass but may be other fabrics such as those formed of threads or yarns of graphite, organic polymers (such as nylon, polyolefins, or acrylics), or natural fibers (like cotton or linen). The fabric may have a very loose weave (such as 0.5 openings per square centimeter) to a rather tight weave (such as thirty openings per square centimeter). The fabric is preferably a simple weave but may be knitted or woven in other known manners. The fabric is precoated with an active thermal protective material which, when exposed to hyperthermal conditions, intumesces, sublimes, or preferably does both.

These variations are merely illustrative.

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Claims

1. A method of treating fiberglass fiber to increase its resistance to heat, the method comprising treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the fiber to at least 1000° C.

2. The method of claim 1 wherein the fiber is formed into a fabric before it is treated.

3. The method of claim 2 wherein the acid mixture further comprises at least one other mineral acid.

4. The method of claim 3 wherein the acid mixture comprises hydrochloric acid.

5. The method of claim 1 wherein the fiber is E-glass.

6. The method of claim 1 wherein the fiber is soaked in an acid bath for a period in excess of twenty-four hours.

7. The method of claim 2 comprising a further step of treating the fabric with a low viscosity resin after the acid treatment step.

8. The method of claim 7 wherein the resin is a silicone oil.

9. The method of claim 8 wherein the silicone oil is a water in oil emulsion.

10. A composite material comprising at least one layer containing a thermoplastic, the layer having embedded therein a fabric, the fabric being coated with an active thermal protective material selected from the group consisting of subliming materials and intumescing materials.

11. The composite of claim 10 wherein the coated fabric comprises an open mesh having from 0.5 to 30 openings per square centimeter, the thermoplastic in the layer extending into the openings and forming a mechanical lock with the coated fabric.

12. The composite of claim 10 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.

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13. The composite of claim 10 wherein the active thermal protective material leaves openings in the weave of the fabric, the thermoplastic material extending into the openings and forming a physical lock with the coated fabric.

14. A container formed of the composite of claim 10.

15. The container of claim 14 wherein the container is a structural automotive container selected from the group consisting of trunk bases and fuel tanks.

16. A structural automotive component having a bottom and an upstanding wall, the pan being formed of the composite material of claim 10.

17. The component of claim 16 wherein the mesh is on a lower side of the bottom and the outside of the upstanding wall.

18. The component of claim 17 wherein the fabric mesh is a single piece of material extending across the bottom and up at least a part of the upstanding wall.

19. The component of claim 16 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.

20. The component of claim 19 wherein the fabric comprises fiberglass fiber having a softening point above about 1000° C.

21. The component of claim 20 wherein the fabric has been treated with a mixture of acids comprising at least 15% sulfuric acid.

22. The component of claim 16 wherein the component is a trunk base.

23. The component of claim 16 wherein the component is a fuel tank.

24. The component of claim 16 wherein the component is an inverted pan formed in part of thermoplastic-coated fibers, the fabric mesh being embedded in an inside surface of the pan.

25. A method of forming a composite structure comprising a step of coating a fabric with an active thermal protective material selected from the group consisting of subliming and intumescing materials, and thereafter a step of softening a resin component of a substrate and embedding the coated fabric in the softened resin.

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26. The method of claim 25 wherein the substrate is a sheet, and wherein the sheet and the fabric are formed into a structure simultaneously with the step of embedding the fabric in the sheet.

27. The method of claim 25 wherein the active thermal protective material leaves openings in the weave of the fabric, the softened resin extending into the openings and forming a physical lock with the coated fabric.

28. A composite material comprising at least one layer of thermoplastic having embedded therein a fabric produced by the method of claim 2.

29. A composite material comprising at least one layer of thermoplastic having embedded therein fibers produced by the method of claim 1.

30. A thermal protective composition having dispersed therein fibers produced by the method of claim 1.

31. In combination, a thermal protective material and a fiberglass fabric embedded therein, the fabric having been treated by the method of claim 2.

32. The combination of claim 31 wherein the thermal protective material is a coating applied to a substrate.

33. The combination of claim 31 wherein the thermal protective composition is preformed into a self-supporting structure.

34. A method of protecting a substrate from fire or thermal extremes comprising applying to the substrate an uncured thermal protective material selected from the group consisting of intumescent materials and subliming materials, and thereafter a step of embedding in the thermal protective material a fiberglass fabric produced by the method of claim 2.

35. A structure comprising an organic resin having embedded therein a fabric, the fabric being precoated with an active thermal protective material selected from the group consisting of subliming and intumescing materials.

36. The structure of claim 35 wherein the organic resin is a polyolefin.

37. A method of treating fiberglass fiber to give it superior high temperature resistance and texture, the method comprising treating the fiber with acid and

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thereafter soaking the fiber in a water-in-oil emulsion of low viscosity organo-metallic oil to fill pores in the glass.

38. The method of claim 37 wherein the low viscosity organo-metallic oil is a low molecular weight silicone oil.

39. The method of claim 38 wherein the silicone is dimethyl polysiloxane.

40. The method of claim 37 wherein the step of treating the fiber with acid comprises treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the fiber to at least 1000° C.

41. A method of forming a composite structure comprising a step of treating a fabric with an active thermal protective material selected from the group consisting of subliming and intumescing materials, a step of placing the treated fabric in a mold, and a step of forming a substrate into a shape in the mold containing the treated fabric.

42. The method of claim 41 wherein the substrate comprises a thermoplastic resin, the step of forming the substrate comprising heating the resin at least to a softening temperature, the treated fabric bonding to the softened resin.

43. The method of claim 41 wherein the substrate is heated to a temperature below an activation temperature at which the active thermal protective material intumesces or sublimes.

44. The method of claim 41 wherein the fabric comprises fiberglass.

45. The method of claim 41 wherein the substrate comprises a felted material.

46. The method of claim 41 wherein the coated fabric includes windows therein, the substrate extending through the windows to lock the coated fabric to the substrate.

47. The method of claim 41 wherein the structure is an automotive trunk base, or trunk liner, or fuel tank.

48. The method of claim 41 wherein the resin comprises a polyolefin.

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49. A composite structure comprising a substrate, the substrate being formed at least in part of a thermoplastic material, and a thermal protective structure adhered to the substrate, the thermal protective structure comprising a fabric coated with an active thermal protective material, the thermal protective material being selected from the group consisting of subliming and intumescing materials, the substrate adhering chemically and mechanically to the pretreated mesh fabric.

50. The structure of claim 49 wherein the thermal protective structure is adhered to the substrate by the thermoplastic material.

51. The structure of claim 49 wherein the thermal protective structure is embedded in the thermoplastic material.

52. A composite structure comprising a substrate, the substrate being formed at least in part of a polyolefin, and a mesh fabric treated with an active thermal protective material, the thermal protective material being selected from the group consisting of subliming and intumescing materials, the treated mesh fabric having from 0.5 to 30 openings per square centimeter, the resin adhering chemically and mechanically to the pretreated mesh fabric.

53. The structure of claim 52 wherein the polyolefin is polypropylene.

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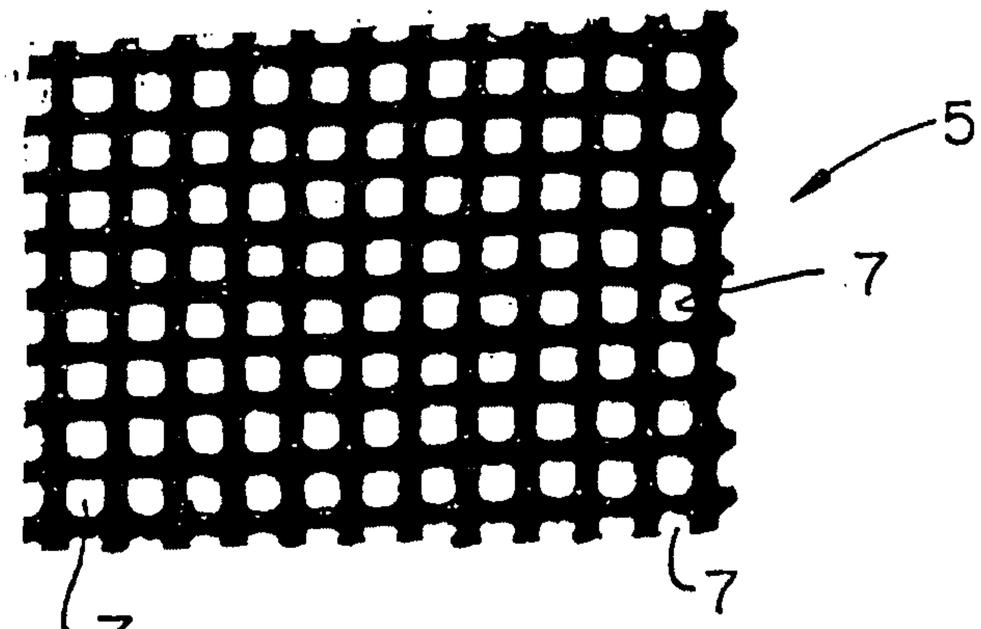


FIG. 1

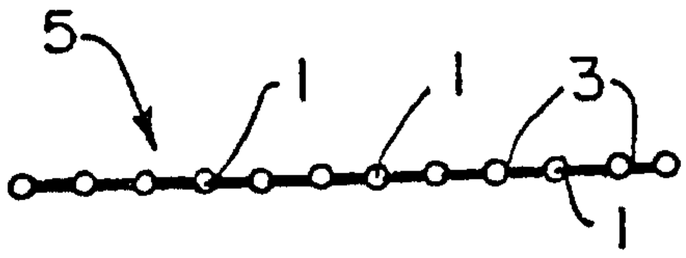


FIG. 2

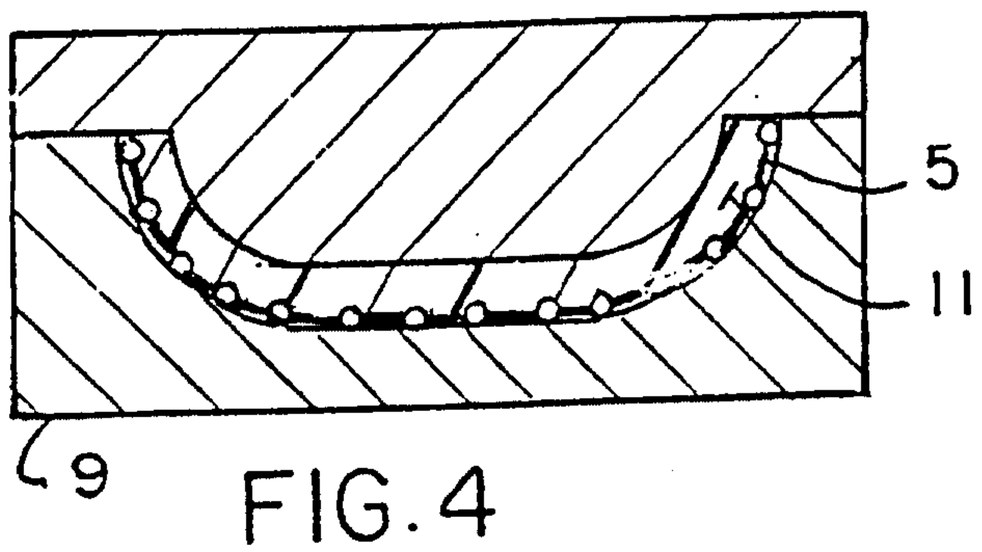


FIG. 4

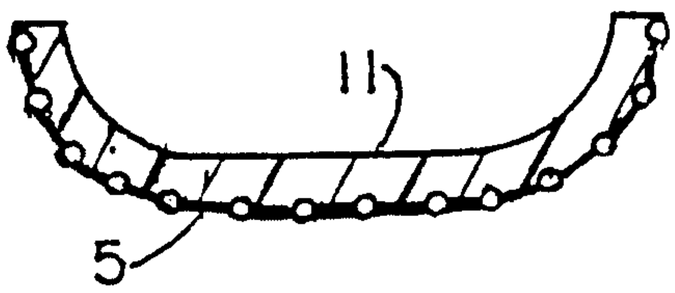
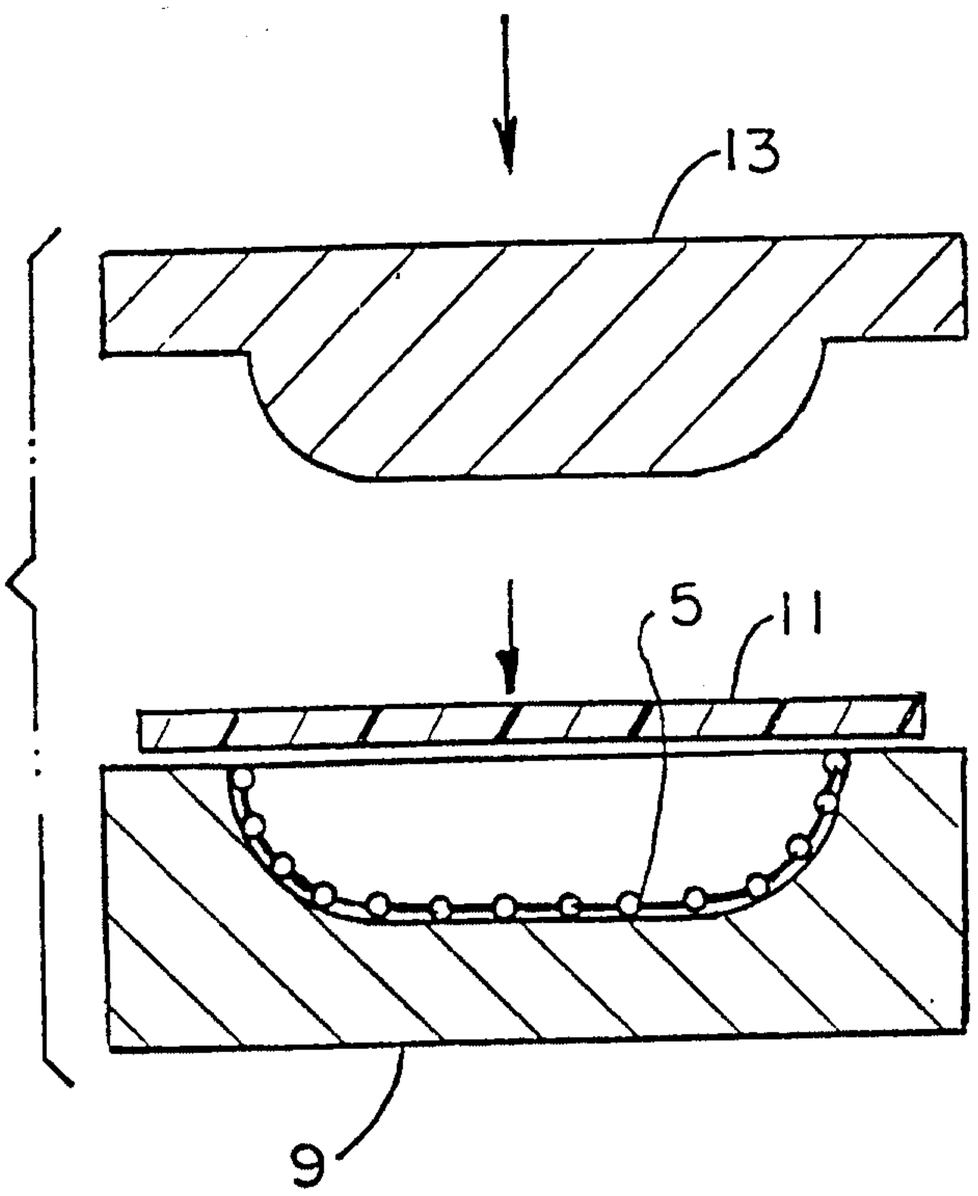


FIG. 5

FIG. 3



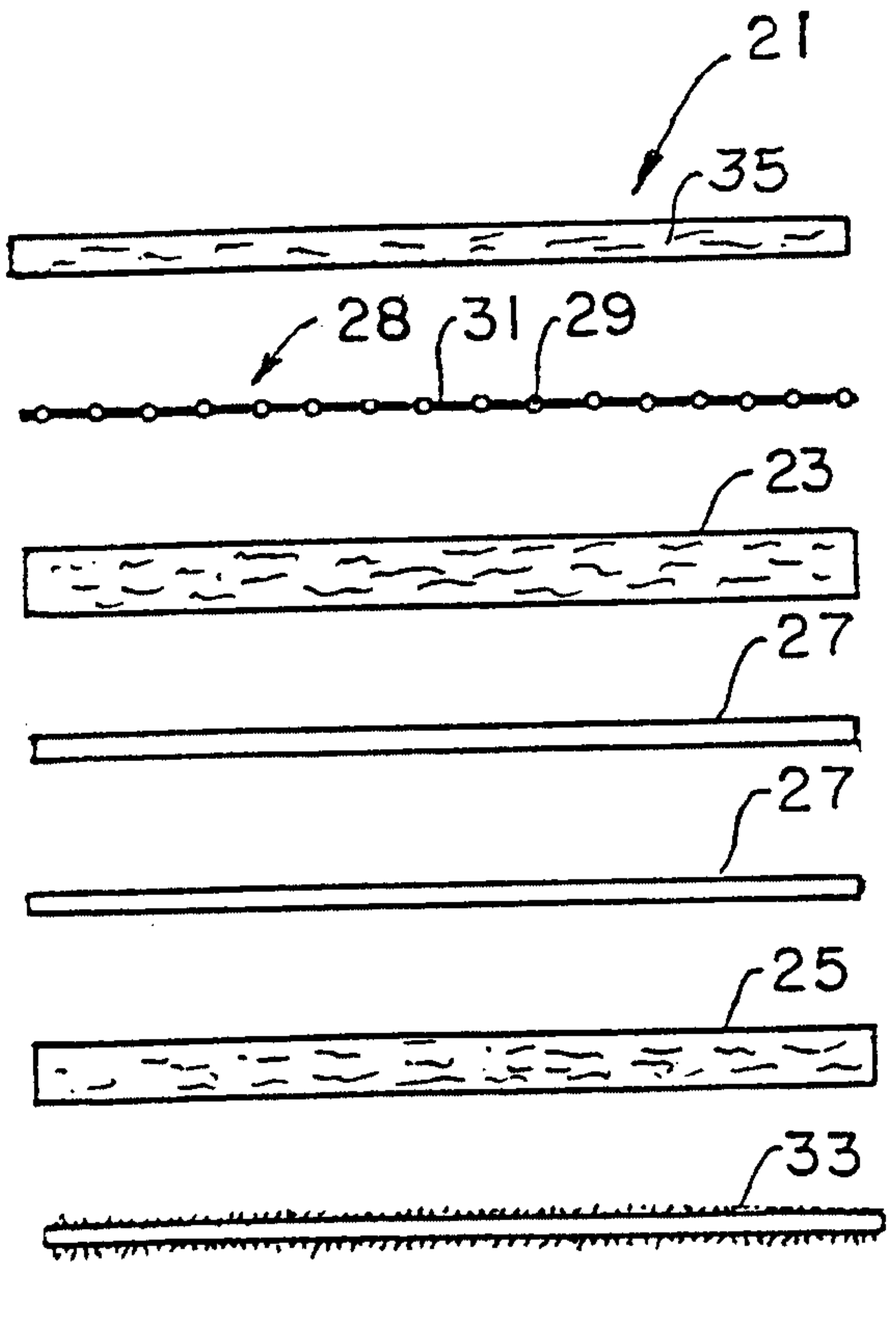


FIG. 6