High density structural (“blocking”) materials composed of a polyimide filled with glass microballoons and methods for making such materials. Structural components such as panels which have integral edgings and/or other parts made of the high density materials.

20 Claims, 3 Drawing Figures
The invention described herein was made in the performance of work under NASA Contract No. NAS9-15484 and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958 (72 Stat. 435; 42 USC 2457).

This application is a division of application Ser. No. 186,563 filed Sept. 12, 1980.

In one aspect our invention relates to structural materials and, more specifically, to novel, improved structural materials composed of a polyimide resin loaded or filled with glass microballoons. We identify such compositions by the term "blocking material."

The invention also relates to novel, improved structural components such as panels composed at least in part of blocking materials having the character described above.

Copending application Ser. No. 186,629 filed Sept. 12, 1980, is concerned in part with the fabrication of novel, improved, low density, structural components such as panels from polyimide resins compounded with fillers such as glass fibers and microballoons and typically sandwiched between two sheets of glass fabric.

We have since discovered that, if glass microballoons of a particular size are employed as a filler in such compositions and in appropriate amounts, a high density, even almost solid material can be obtained. Such materials are particularly useful as panel edgings and in other applications where attachment of one component to another is involved because of the high resistance they offer to the direct withdrawal of threaded fasteners such as screws.

Exemplary of the polyimides that can be employed in these novel blocking materials are the copolymers described in U.S. Pat. No. Re. 30,213 and the terpolymers described in application Ser. No. 186,668 filed Sept. 12, 1980. That application was copending with parent application Ser. No. 186,563 but has since been abandoned.

The patented copolymers are derived from precursors which, in their preferred forms, are essentially equimolar mixtures of a lower alkyl half ester of 3,3',4,4'-benzophenonetetraacarbocyclic acid and two primary diamines. One of the diamines is a heterocyclic diamine, and the other is an aromatic meta- or para-substituted diamine which is free of aliphatic moieties. A ratio of 0.4 to 0.6 mole of heterocyclic diamine per mole of 3,3',4,4'-benzophenonetetraacarbocyclic acid ester is preferred. However, precursors having a heterocyclic diamine/acid ester ratio of 0.3 have also successfully been employed.

The terpolymers described in application Ser. No. 186,668 differ chemically from the copolymers just described in that they are made from precursors which include an aliphatic diamine in addition to the aromatic and heterocyclic diamines employed in the copolyimide precursors.

From 0.05 to 0.3 mole of aliphatic diamine per 1.0 mole of benzophenonetetraacarbocyclic acid ester can be employed, and from 0.1 to 0.3 mole of heterocyclic diamine per mole of ester can be used.

Exemplary of the aromatic and heterocyclic diamines that can be employed in the just described copolyimides and terpolymides are:

- 2,6-diaminopyridine
- 3,5-diaminopyridine
- 3,3'-diaminodiphenyl sulfone
- 4,4'-diaminodiphenyl sulfone
- 4,4'-diaminodiphenyl sulfide
- 3,3'-diaminodiphenyl ether
- 4,4'-diaminodiphenyl ether
- meta-phenylene diamine
- para-phenylene diamine
- p,p'-methylenediamine
- 2,6-diamino toluenes
- 2,4-diamino tolune

Many other aromatic and heterocyclic diamines have been described in the open and patent literature dealing with the making of polyimides—see, for example, U.S. Pat. Nos. 3,179,614 issued Apr. 20, 1965, to Edwards; 3,575,891 issued Apr. 20, 1971, to LeBlanc et al; and 3,629,180 issued Dec. 21, 1971, to Yoda et al. Aromatic and heterocyclic diamines selected from those listed in the literature can also be utilized in copolyimides and terpolymides of the character described above.

Aliphatic diamines having from three to 12 carbon atoms have been employed in the terpolymides. However, diamines having more than six carbon atoms will typically prove preferable. Also, aliphatic diamines with even numbered chains are preferred.

Aliphatic diamines we have used include:
- 1,3-dimino propane
- 1,4-diminobutane
- 1,6-dimino hexane
- 1,8-dimino octane
- 1,12-dimino decane

and Jeffamine 230. The latter is available from the Jefferson Chemical Company and has the formula:

\[
\begin{align*}
&\text{H}_2\text{N}-\text{C} \quad \text{O} - \text{C} \quad \text{C} - \text{NH}_2 \\
&\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]

where \(x\) is approximately 2.6.

The precursors of the polyimides with which we are concerned are prepared by first reacting 3,3',4,4'-benzophenonetetraacarbocyclic acid (or, preferably, its dianhydride) with an esterification agent to form an alkyl diester or half ester. Exemplary esterification agents are methyl, ethyl, propyl, and isopropyl alcohols. Methanol is in many cases preferred because of its widespread availability, low cost, and other attributes and because its use facilitates conversion of the precursor to a polyimide.

Ethanol is also a preferred esterification agent.

The esterification reaction is followed by the addition of the diamine or diamines, which are dissolved in the reaction mixture. The temperature is kept below the reflux temperature of the esterification agent during dissolution of the diamines and low enough to avoid polymerization of the diamines and ester.

The essentially non-polymeric, "liquid resin" polyimide precursor that results is typically diluted with the same alcohol employed as an esterification agent in a ratio of 20 parts of alcohol per 100 parts of resin (phr) in the case of copolyimide systems and at a phr of 30 when terpolyimide systems are involved. This diluted resin is compounded with the glass microballoons, typically in a variable speed mixer, producing a formulation with a pastelike consistency.

For our purposes we employ from 5 to 50 percent of the microballoons based on the weight of the polyimide...
3 into which the precursor is ultimately converted. On
the order of 30 weight percent of the microballoon filler has
proven optimum for one polyimide system which
will be described in more detail below.

Additives may also be incorporated in the blocking
material to alter or control the properties of the block-
ing material formulation. One that is particularly useful
is a cross linking agent. From 10 to 20 weight percent of
an agent of that character materially increases the hy-
drolytic stability of the blocking material.

The particular kind of microballoons employed in the
blocking material formulation is not critical although
they should be in the range of 0.07 to 0.12 mm in diame-
ter to provide the wanted resistance to screw with-
drawal. 3M Company type C-15X glass microballoons
have proven satisfactory.

The initial step in converting the precursor-filler
formulation to a blocking material is to spread it on a
suitable support or substrate in an appropriate thickness.

Next, the artifact this produces is dried. That may be
done by heating the artifact in a circulating air oven,
typically at a temperature in the range of 70° to 93° C.
(160° to 200° F.) until an optimum 29 to 31 percent of the
solvent alcohol has been evaporated.

The dried artifact is heated to develop a cellular
physical structure in which the filler is uniformly dis-
tributed and a polyimide chemical structure from the
precursor.

Thermal heating may be employed for these pur-
poses. Temperatures of 230° to 315° C. (446° to 600° F.)
for periods of 15 to 30 minutes have proven capable of
foaming and curing the precursor. Another regime that
has proven satisfactory involves heating the formula-
tion first at a temperature of 104° to 163° C. (220° to
325° F.) for 15 to 20 minutes to develop the foam and
then at a temperature of 288° to 315° C. (550° to 600° F.)
for 30 to 60 minutes to cure it.

Alternatively, the foaming and curing of the precu-
 sor or those and the drying step can be accomplished by
microwave heating.

Foaming-curing parameters that have proven satis-
factory in converting representative precursors are two
12 minutes exposure to high frequency radiation in an
oven operating at a frequency of 915 to 2450 mHz
and at a 3.75 to 15 kW power output and a power output to
precursor weight ratio of 0.6 to 1 kW/kg.

Drying can be carried out as an earlier stage in the
same oven using a power output of 1.25 to 2.5 kW, also
for 2 to 12 minutes, to reduce the volatiles content of the
polyimide precursor-microballoon formulation by the
optimum 29 to 31 percent.

Steady application of the microwave energy is not
required, and pulsed or cyclic exposure of the precursor
to the microwave energy may even product superior
results. Typically, the duration of the microwave energy
pulses and of the intervals therebetween will be on
the order of 60 and 20 seconds, respectively.

Also, conductive fillers can often advantageously be
incorporated in the precursor to promote its conversion
to a polyimide by generating additional thermal energy.
From 5 to 20 weight percent of activated carbon or
graphite can be employed for that purpose.

Similarly, an optimum product can in many, if not
most, cases be obtained by heating the substrate or mold
on or in which the precursor is foamed to a temperature
of 121.1° to 148.9° C. (250° to 300° F.) before the pre-
cursor is exposed to microwave energy.

Another technique that can be used to advantage in
making blocking materials and structural components
including such materials by the practice of the present
invention is thermal heating of the microwave cavity.

Temperatures in the range of 121.1° to 232.2° C. (250°
5 to 450° F.) are employed.

In addition, the microwave heating step or steps can
often be followed to advantage by a thermal postcure of
the polyimide. This is accomplished by heating the
product of the microwave heating step in a circulating
air oven at a temperature of 500° to 550° F. for 30 to 200
minutes.

The microwave techniques for heating the precursor
require that a substrate or mold material which is com-
patible with the microwave radiation be employed. If a
mold technique is used, the material must also have
sufficient flexural strength to withstand the pressure of
the expanding foam. Substrate and mold materials that
have been found suitable include Ridout Plastics Com-
pany polypropylene lined with a Teflon-coated glass
(Taconic 7278); Pyroceram (a Corning Glass crystalline
ceramic made from glass by controlled nucleation); and
glass filled polyimides. Other materials possessing the
necessary attributes discussed above can also be em-
ployed.

It was pointed out above that the blocking material
can be made as an integral edging or other part of a struc-
tural component such as a panel.

In one exemplary process for making panels with
integral portions of blocking material in accord with the
principles of our invention, the pastelike formulation of
polyimide resin and glass microballoons is again spread
on a suitable support, typically in a hollow rectangle
on top the compounded resin.

The initial step in converting the precursor-filler
formulation to a blocking material is to spread it on a
suitable support or substrate in an appropriate thickness.

Next, a liquid resin polyimide precursor as described
above and compounded with selected fillers is spread
on glass cloth (e.g., Owens Corning Style 120) wet with
the resin in the hollow rectangle formed by the blocking
material formulation. A second resin wetted glass cloth
is placed on top the compounded resin.

The resulting assembly is dried, again as described
above; sandwiched between sheets of a microwave
compatible material; and processed first in a microwave
oven and then by thermal postcuring or processed by
thermal heating, all as described above.

Various fillers including carbon mats, glass strands,
rovings, and microballoons and E. I. DuPont de Ne-
mours and Company Kevlar and Nomex fibers can be
employed in panels made by the techniques just de-
scribed. From 5 to 40 weight percent of filler based on
the weight of the ultimately formed polyimide can be
used, depending upon the physical properties wanted in
the panel and the particular filler that is used.

Other additives such as cross linking agents can be
added to the resulting composition to impart wanted
properties to the final product. A surfactant can also be
added to increase fatigue resistance and to increase the
bubble stability of the polyimide and the uniformity of
the cellular structure.

One preferred surfactant is FS-B, a nonionic, fluori-
nated, polyalkylene copolymer manufactured by E. I.
DuPont de Nemours and Company.

Other surfactants that have been successfully em-
ployed are FS-C, AS-2, and X-3, nonionic surfactants of
the same general chemical composition as FS-B and
manufactured by the same company, and L-530, L-
5410, and L-5430, which are silicone surfactants manufactured by Union Carbide Company. We employ from 0.015 to 1.5 percent of surfactant based on the weight of the ester and diamine constituents.

We do not claim that either blocking materials or polymeric compositions filled with glass particles of spherical configuration are categorically novel.

The previously proposed blocking materials of which we are aware, however, are polyurethane based. They consequently are highly flammable, and they further give off toxic fumes as they burn. Our novel blocking materials, in contrast, are high temperature resistant; and they are capable of undergoing oxidative degradation without generating toxic products or smoke.

U.S. Pat. No. 3,947,388 issued May 23, 1974, to Ohkawa et al is believed by us to be representative of those prior art patents dealing with glass sphere filled polymers.

The Ohkawa et al materials, intended for applications where light reflecting capability is important, contain glass beads having diameters in the 1 to 2 mm range. They are consequently not blocking materials; the relatively large beads would afford little resistance to screw withdrawal.

Furthermore, Ohkawa et al is not concerned with polyimide-based systems at all, let alone with the particular systems of that character utilized by us.

The particular polyimide systems we employ and the particular techniques we employ for making blocking materials and structural components containing such materials also distinguish our inventions from the microballoon filled polyimides disclosed in U.S. Pat. No. 3,761,430 issued Sept. 25, 1973, to Witzel.

The Witzel polymers are derived from unsaturated bisimides, not tetracarboxylic acid diesters; and the filler is compounded with the polymer, not its essentially non-polymeric precursor as is the case in our process. Furthermore, Witzel is concerned with fillers capable of imparting specified electrical characteristics to his polymers, not resistance to screw withdrawal.

The reader will realize, from the foregoing, that important and primary objects of our invention reside in the provision of novel, improved blocking materials and in the provision of processes for making such materials.

Other important, and primary, objects of the invention reside in the provision of novel, improved structural components in which those materials are integrated and in the provision of methods for making the structural components.

Yet other important, but more specific, objects of our invention reside in the provision of blocking materials which are temperature resistant and capable of undergoing oxidative degradation without generating smoke or toxic products;

which can be fabricated readily, and relatively economically, as such or as integral parts of structural components; and

which are derived from tetracarboxylic acid diester-/diamine-based, polyimide precursors compounded with glass microballoons.

Still other important, specific objects of our invention are the provision of structural components of the character identified above:

which overall have a relatively low density but can nevertheless be easily and securely fastened to other components;

which are light in weight but strong and rigid and can accordingly be used as flooring and in other demanding applications;

which are fire resistant and hydrolytically stable;

which are durable;

which can be manufactured economically and with relative ease in large sizes.

Still other important objects of the invention are the provision of methods for manufacturing blocking materials and structural components of the character described above which are suitable for large scale production and are versatile, allowing the blocking materials and structural components to be produced in a wide variety of forms with widely varying mechanical, thermal, and other properties.

Other important objects and features and additional advantages of our invention will become apparent to the reader from the foregoing and the appended claims.

Still others will become apparent as the ensuing description and discussion of our invention proceeds in conjunction with the accompanying drawing in which:

FIG. 1 is a section through a panel fabricated in accord with the principles of the present invention; the panel has edgings of a blocking material embodying and made in accord with those principles;

FIG. 2 pictorially illustrates a blocking material in accord with the principles of the present invention; and

FIG. 3 similarly depicts a rigid panel with which has edgings of blocking material embodying, and is fabricated in accord with the principles of, our invention.

Referring now to the drawing, FIG. 1 depicts a multiple density wall panel 10 constructed in accord with the principles of the present invention.

Panel 10 has an outer frame or edging 12 of blocking material, a low density core 14, and a rib 16 also made of the blocking material. The panel can be attached to structural supports by installing threaded fasteners in the apertures 18 provided in edging 12 and rib 16.

Examples detailing the manufacture of representative blocking materials that might be found in edging 12 and rib 16 and the fabrication of a panel such as that illustrated in FIG. 1 follow.

A representative polyimide system that can be employed both in our blocking materials and in the cores of structural components incorporating such materials is our 1702-1.

The 1702-1 precursor was prepared by adding 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (322.2 g, 1.0 mole) to 240 ml of methyl alcohol and 24 ml of H2O in a one-liter, three-neck flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser. After addition, the mixture was heated and refluxed until clear. The mixture was then refluxed for an additional 60 minutes to ensure complete esterification of the acid to its half ester.

The reaction mixture was cooled to 40°-50° C. (104°-122° F.).

2.6 Diaminopyridine (32.8 g, 0.3 mole) and p-p'thylene diamine (138.7 g, 0.7 mole) were added to the half ester solution, and the mixture was heated at 60°-65° C. (140°-149° F.) for five minutes to dissolve the diamines.

To make a blocking composition, the resulting liquid resin was diluted with 20 phr of methyl alcohol and compounded with 30 percent of C-15X microballoons in an ABBE double shaft mixer.
This produced a formulation of pastelike consistency which was spread at a loading of 2.05 kg/m² (0.42 lbs/ft²) on an aluminum foil support.

Excess solvent was removed by heating the material in a 5 kW Gerling Moore Batch Cavity Model 4115 Microwave Oven on a sheet of Teflon-coated glass cloth at a power output of 1.25 kW for a period of 3–5 minutes.

Foaming was carried out in the microwave oven at a power output of 5.0 kW for six minutes between two sheets of Pyroceram.

The samples were cured in a Blue M circulating air industrial oven at a temperature of 287.7°C (550°F) for 30 minutes.

A screw withdrawal test was made of the resulting blocking material to demonstrate its utility using the protocol and equipment specified in ASTM Standard D-1761.

The results are compared with the specifications the blocking material was intended to meet in the following table:

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Screw Withdrawal Test of Blocking Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density (kg/m²)</td>
</tr>
<tr>
<td>Actual</td>
<td>16</td>
</tr>
<tr>
<td>Spec.</td>
<td>16</td>
</tr>
</tbody>
</table>

Specimens were also tested for machinability. In these tests feather edges were generated without difficulty.

A representative sample of this blocking material is shown in FIG. 2.

We subsequently ascertained that the just described blocking material absorbed water to an extent that might rule out its use in applications where hydrolytic stability is required.

The problem was approached by adding varying amounts of Imperial Chemical Company L-170 cross linking agent to the liquid resin-glass microballoon formulation, the procedure for drying, foaming, and curing the formulation remaining the same.

Water absorption of the modified blocking material was measured in accord with ASTM Standard D 2829-69 (1975) except that the underwater weighing rig called for in that specification was not employed.

The resulting panel with its low density core and edging of screw withdrawal resistant blocking material is shown in FIG. 3.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description; and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by U.S. Letters Patent is:

1. A process of making a structural component which includes the steps of assembling in a juxtaposed relationship a core material and a formulation that is convertible into a blocking material, said core material and said formulation each containing a polyimide precursor prepared by dissolving one or more primary diamines and 3,3',4,4'-benzophenonetetracarboxylic acid or an anhydride of that acid in essentially stoichiometric amounts in a lower alkyl alcohol, said formulation also including at least one filler, and the assembly being heated until said precursors are converted to polyimides and said blocking material is integrated with said core material.

2. A process of making a structural component as defined in claim 1 wherein at least one of the polyimide precursors contains two primary diamines, one of said diamines being heterocyclic and having nitrogen in the ring, the other of said diamines being a para- or meta-substituted aromatic diamine which is free of aliphatic moieties, and said heterocyclic diamine being present in said precursor in a ratio of 0.3 to 0.6 mole of that diamine per mole of 3,3',4,4'-benzophenonetetracarboxylic acid ester.
3. A process of making a structural component as defined in claim 1 wherein at least one of the polyimide precursors contains three primary diamines, one of said diamines being heterocyclic and having nitrogen in the defined in claim ring, another of said diamines being a para- or meta-substituted aromatic diamine which is free of aliphatic moieties, the third of said diamines being aliphatic, and said precursor containing from 0.05 to 0.3 mole of aliphatic diamine and from 0.1 to 0.3 mole of heterocyclic diamine per mole of 3,3',4,4'-benzophenonetetracarboxylic acid ester.

4. A process of making a structural component as defined in claim 3 wherein the aliphatic diamine in the precursor has from three to twelve carbon atoms.

5. A process of making a structural component as defined in claim 3 wherein the aliphatic diamine in the precursor has the formula:

\[
\begin{align*}
&\text{H} \quad \text{H} \\
&\text{H} \quad \text{C} \quad \text{O} \quad \text{C} \\
&\text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]

where x is on the order of 2.6.

6. A process of making a structural component as defined in either of the preceding claims 1 to 3 wherein the aromatic and heterocyclic diamines in the precursors are selected from the following group:
- 2,6-diaminopyridine
- 3,5-diaminopyridine
- 3,3',4,4'-benzophenonetetracarboxylic acid
- 4,4'-diaminodiphenyl sulfone
- 4,4'-diaminodiphenyl sulfide
- 3,3'-diaminodiphenyl ether
- 4,4'-diaminodiphenyl ether
- meta-phenylene diamine
- para-phenylene diamine
- p,p'-methylenedioxy dianniline
- 2,6-diamino toluene
- 2,4-diamino toluene.

7. A process of making a structural component as defined in claim 1 wherein the precursors are converted to polyimides by heating said assembly at a temperature of 230° to 315° C. for 15 to 30 minutes.

8. A process of making a structural component as defined in claim 1 wherein the precursors are converted to polyimides by heating said assembly first at a temperature of 104° to 163° C. for 15 to 30 minutes and then at a temperature of 288° to 315° C. for 30 to 60 minutes.

9. A process of making a structural component as defined in claim 1 wherein said precursors are converted to polyimides by exposing said assembly to microwave radiation for 2 to 12 minutes at a power output of 3.75 to 15 kW.

10. A process of making a structural component as defined in claim 9 which employs a microwave radiation power output to unit weight of polyimide precursor in the range of 0.6 to 1 kW/kg.

11. A process of making a structural component as defined in claim 9 wherein the assembly is exposed to pulses of microwave radiation, the duration of the pulses and of the intervals therebetween being on the order of 60 and 20 seconds, respectively.

12. A process of making a structural component as defined in claim 9 wherein said precursor is exposed to microwave radiation in a microwave cavity and wherein the cavity is heated to a temperature of at least 250° F. and less than 450° F. while the assembly is exposed to said microwave radiation.

13. A process of making a structural component as defined in claim 9 wherein a conductive filler is admixed with said precursors prior to exposing said assembly to microwave radiation to promote the conversion of the precursors to polymeric materials.

14. A process of making a structural component as defined in claim 9 wherein the materials produced by exposing the precursors to microwave radiation are thereafter post cured by heating said assembly at a temperature on the order of 250° to 550° F. for 40 to 200 minutes.

15. A process of making a structural component as defined in claim 9 wherein, while said assembly is exposed to microwave radiation, it is supported on or confined by an inflexible, temperature resistant material that is compatible with such radiation, said material being a polypropylene lined with a fluorocarbon polymer coated glass, a glass based crystalline ceramic, or a glass filled polyimide.

16. A process of making a structural component as defined in claim 9 wherein the precursors are converted to polyimides by exposing said precursors to microwave radiation, said material being a polypropylene lined with a fluorocarbon polymer coated glass, a glass based crystalline ceramic, or a glass filled polyimide.

17. A process of making a structural component as defined in claim 1 which includes the step of sandwiching the core material between skins of woven glass fabric reinforcement to thereby enhance the physical properties of the component.

18. A process of making a structural component as defined in claim 1 wherein the core material contains from 5 to 40 weight percent of filler based on the weight of the polyimide into which the precursor of the core material is converted.

19. A process of making a structural component as defined in claim 1 wherein said precursors are diluted with a lower alkyl alcohol solvent in a ratio of 20 parts to 30 parts of solvent per 100 parts of precursor prior to mixing the filler or fillers therewith and wherein the resulting mixtures are both exposed to microwave energy at a power output of 1.25 to 2.5 kW or thermally heated until from 29 to 31 percent be weight of the solvent based on the weight of each mixture has been evolved therefrom prior to converting said precursors to polyimides.

20. A process of making a structural component as defined in claim 1 wherein said structural component is assembled and processed prior to the heating step(s) in which the polyimide precursors are converted to polyimides by disposing said blocking material formulation on a substrate, drying the blocking material formulation, placing a fabric reinforcement on said substrate, spreading the core material on said fabric, placing a second fabric reinforcement on said core material, and drying the resulting assembly.