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FIRE RESISTANT PIPE

Field of the Invention

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The present invention relates generally to fire resistant pipe and pipe fittings and, more particularly, to a filament wound fiber-reinforced pipe and pipe fittings having one or more surrounding fiber-reinforced resin impregnated layers, which display enhanced fire resistance, burst strength, and impact resistance when compared with conventional fiber-reinforced pipes and pipe fittings.

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Background of the Invention

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Pipes and pipe fittings formed from fiber-reinforced plastics have gained widespread acceptance as viable alternatives to their steel counterparts in such applications where cost, weight, and/or chemical resistance is a concern. Conventional fiber-reinforced plastic pipes include a filament component that is wound on a mandrel, and a resin component that is used to bond the filament windings together. The filament winding acts to structurally reinforce the otherwise resin pipe by providing a desired degree of hoop and longitudinal strength to the pipe. The fiber and resin components are selected for one or more desired physical properties, making the pipe particularly adapted to a specific application. Polyester and epoxy resins are typically favored for use in forming such pipes and pipe fittings because of their good weatherability, corrosion, and chemical resistance.

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Fiber-reinforced plastic pipes and pipe fittings are used in applications where some degree of temperature resistance is desired as well as weather, corrosion and chemical resistance. An example of one such application is fire fighting piping that is used in industrial plants, offshore platforms and the like. Typically, pipes and pipe fittings used in fire fighting piping must be designed to accommodate and deliver a desired pressure of water, or other fire fighting liquid, foam, or foam/liquid mixture, when subjected to high temperature conditions or when placed in close flame vicinity. Fiber-reinforced plastic pipes are favored for use as fire fighting piping on off-shore oil platforms and are typically maintained in an empty or uncharged state until a fire is detected. Once a fire is detected, water is routed to the pipes at pressures that can be as high as 225 psig (16 Kgf/cm²), depending on the rated pressure for the pipe. Accordingly, fiber-reinforced pipes that are used in such applications must be able to withstand an elevated temperature and/or close flame contact for a brief period of time when empty, i.e., without the benefit of being charged with water and having the water act as a heat transfer medium to minimize detrimental temperature effects.

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Fiber-reinforced plastic pipes used in such fire fighting pipe applications include those made from epoxy resin because of their enhanced corrosion resistance. A rigorous test has been devised to qualify fiber-reinforced pipes for use in such fire fighting pipe applications.

1 The test requires placing the pipe and pipe fitting assembly in close vicinity to a 1,000°C
flame with the pipe dry for a period of five minutes, and then filling the pipe with water at
a rated pressure for approximately twenty minutes. To pass the test, the pipe and pipe
fittings assembly must not show any signs of structural damage and only minor leakage.
5 Fiber-reinforced plastic pipes and pipe fittings formed from epoxy resin have been shown to
display significant temperature induced deterioration at temperatures as low as 120°C and,
therefore, have proven incapable of passing the test. Fiber-reinforced pipes and pipe fittings
formed from polyester resin are equally incapable of passing the test, as these pipes have
been demonstrated significant temperature induced deterioration at temperatures as low as
10 94°C.

In order to pass the test, fiber-reinforced plastic pipes formed from epoxy resin can
be coated with an intumescent coating, or formed from an intumescent containing epoxy
resin. When exposed to high-temperature conditions or flame contact, the intumescent
coating foams, forming a temperature insulating barrier that serves to protect the underlying
15 pipe surface. However, a disadvantage of using an intumescent coating is that it increases
the expense of the fiber-reinforced plastic pipe, thereby reducing the cost incentive for using
the pipe, and generates toxic smoke when subjected to flame contact.

An alternative for using intumescent coated fiber-reinforced epoxy pipes in fire
fighting pipe applications is to construct the pipe from phenolic rather than epoxy resin,
20 which is known to provide enhanced temperature resistance. However, fire fighting pipes
and pipe fittings made from fiber-reinforced phenolic resin have also been found to be
incapable of passing the test, displaying fiber rupture induced side wall failures when exposed
to rated pressures.

Fiber-reinforced plastic pipes formed from epoxy, polyester and phenolic resins are
25 known to display a limited amount of impact resistance and flexibility. Physical properties
of impact resistance and flexibility are desired in applications such as fire fighting piping and
pipe fittings because it is desired that such piping remain capable of retaining a rated water
pressure even when subjected to some amount of movement, possibly created by falling,
failing or distorting adjacent structures during a fire.

30 It is, therefore, desired that fiber-reinforced resin pipe and pipe fittings be constructed
that are lightweight, weatherable, corrosion resistant, chemical resistant, and have sufficient
burst strength and temperature resistance to pass the above-described test for use in fire
fighting pipe applications. It is desired that the fiber-reinforced resin pipe not produce toxic
smoke when exposed to flame contact, and provide a desired degree of both impact resistance
35 and flexibility. It is also desired that the fiber-reinforced resin pipe be formed from available
materials using conventional manufacturing techniques.

1 **Summary of the Invention:**

 There is, therefore, provided in the practice of this invention fire resistant pipes and pipe fittings that are constructed having sufficient temperature and flame contact resistant to permit their use in such high-temperature applications as fire fighting piping. Fire resistant
5 pipes prepared according to principles of this invention include a structural pipe wall formed from helically wound reinforcing fiber that is bonded together with a thermoset polymer resin. The polymer resin is selected from the group consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures thereof. The helically wound reinforcing fiber is wetted by the resin so that it comprises in the range of from about 10 to
10 40 percent by weight resin. The structural wall is formed from multiple layers of the windings, wherein the number of layers depend on such factors as the desired hoop and longitudinal strength, and temperature resistance desired for a particular pipe application.

 In a first embodiment, a fire resistant layer is applied to the surface of the structural pipe wall. The fire resistant layer is a resin rich layer that acts as a heat ablative shield.
15 The fire resistant layer includes a carrier adapted to accommodate a large amount of a thermosetting polymer resin. The carrier is selected from the group of fibrous mat-like materials that include glass fiber, carbon fiber, nylon fiber, polyester fiber, similar fiber felts, chopped fibers, and combinations thereof. The resin component is selected from the same group of resins previously described for forming the structural pipe wall. It is desired
20 that both resins be compatible, and preferably be the same, to facilitate forming a chemical bond between the structural pipe wall and the fire resistant layer during cure. The fire resistant layer comprises about three times the resin content of the helically wound reinforcing fiber layer.

 In a second embodiment, a number of energy absorbing material layers are disposed
25 around a surface of the structural wall. The energy absorbing material used to form the layers is selected from the group of materials capable of absorbing heat energy from an outside surrounding layer by phase transformation, e.g., to produce a gas, below a degradation temperature of the structural wall. The gas formed by such phase transformation produces a thermally insulating air pocket therebetween.

30 A number of fiber-reinforced resin layers are disposed over the energy absorbing layers. The fiber-reinforced layers can be made from the same or different fiber and resin components used to form the structural wall.

 In a third embodiment, a jacket is disposed around a surface of the structural wall. The jacket is made up of alternating release layers and fiber-reinforced resin layers. The
35 release layers are formed from a material that is incapable of forming a bond with the resin component of the surrounding fiber-reinforced resin layers and/or structural wall to form a disbondment layer therebetween. Such a disbondment layer improves the impact resistance of the pipe because it is energy absorbing to improve impact resistance and reduce thermal

1 stress be preventing the transfer of an impact shock wave from an outside pipe surface to the structural wall.

5 The fire resistant layer in the first embodiment, the energy absorbing material layers in the second embodiment, and the jacket in the third embodiment are each formed having a sufficient wall thickness to protect the structural wall of the pipe or pipe fitting from heat induced degradation caused by exposing the outermost pipe wall to a 1,000°C flame for at least five minutes when the pipe is in a dry condition, i.e., when the pipe is not charged with water.

10 Fire resistant pipes and pipe fittings prepared according to principles of this invention are lightweight, weatherable, corrosion resistant, chemical resistant, and have sufficient temperature resistance to be used in fire fighting pipe applications without suffering temperature or flame contact related failure. Fire resistant pipes of this invention, when exposed to flame contact, do not produce toxic smoke and have enhanced impact resistance and flexibility when compared to conventional fiber reinforced plastic pipes formed from epoxy and polyester resin ingredients.

Brief Description of the Drawings:

20 These and other features and advantages of the present invention will become appreciated as the same becomes better understood with reference to the specification, claims, and drawings wherein:

FIG. 1 is a side elevational view of a first fire resistant pipe embodiment constructed according to principles of this invention prior to application of one or more fire resistant layer(s);

25 FIG. 2 is a side elevational view of the fire resistant pipe of FIG. 1 after application of one or more fire resistant layer(s);

FIG. 3 is a cross sectional view of the fire resistant pipe of FIG. 2 taken across section 3-3;

30 FIG. 4 is a cross sectional view of a second fire resistant pipe embodiment comprising an energy absorbing material layer interposed between a structural pipe wall and an outside fiber-reinforced resin layer;

FIG. 5 is a cross sectional view of an alternative second fire resistant pipe embodiment comprising successive energy absorbing material layers interposed between a structural pipe wall and an outside fiber-reinforced resin layer;

35 FIG. 6 is a perspective view of a third fire resistant pipe embodiment comprising a jacket of repeating release layers and fiber-reinforced resin layers interposed between a structural pipe wall and an outside fiber-reinforced resin layer; and

FIGS. 7A to 7C are elevational side views of fire-resistant pipe fittings constructed according to principles of this invention.

1 **Detailed Description:**

Referring to FIG. 1, a fire resistant pipe 10 constructed according to principles of this invention includes a structural pipe wall 12 formed from multiple layers of helically wound reinforcing fiber 14 bonded together with a resin 16. The structural pipe wall 12 can be
5 formed by using conventional techniques well known in the art for forming fiber-reinforced plastic (FRP) pipe, such as by winding the reinforcing fiber around a mandrel at one or more specific wind angles, and in one or more directions, to obtain a particular degree of hoop and longitudinal strength. In a preferred embodiment, the fiber windings are wound under
10 tension at an angle of approximately 54 degrees around the mandrel in one directions and then in an opposite direction, as this wind angle is known to produce a pipe having an optimum degree of both hoop and longitudinal strength. The number of fiber windings that are used to construct the structural pipe wall depends on the particular size of and application for the pipe. While the above-described technique has been directed toward the construction of pipe, it is to be understood that the same technique can be used to construct pipe fittings
15 such as tees, elbows and the like as well.

The reinforcing fiber component may be selected from conventional filament materials used for forming FRP pipe that do not melt when exposed to fire such as glass, carbon, and the like, and combinations thereof. In a preferred embodiment, the reinforcing fiber is glass. The structural pipe wall is constructed so that a sufficient amount of the resin component is
20 used to wet and bond together the fiber windings. The structural pipe wall may comprise in the range of from about 10 to 40 percent by weight of the resin component. In a preferred embodiment, the structural pipe wall comprises approximately 25 percent by weight resin. The resin is applied to the fiber windings by a conventional application technique, such as by running the windings through a resin bath.

25 The resin component may be selected from the group of resins consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures thereof. Any type of phenolic resin can be used as the resin component and is ultimately selected based on the desired physical properties for the intended end use application. Preferred phenolic resins suitable for use in forming the structural pipe wall include phenolic resole and phenolic
30 novolac resins. Suitable phenolic resins can include those based on phenol, substituted phenols like para-cresol, xylenol, bisphenol A, paraphenylphenol, para-tert-butyl phenol, para-t-octyl phenol and resorcinol. The phenolic resin can be prepared by combining a suitable phenol with an aldehyde, such as formaldehyde, acetaldehyde, paraldehyde, glyoxal, hexamethylene-tetraamine, and furfural.

35 Preferred phenolic resins are low viscosity phenolic resole resins because of their optimal wetting of the fiber-reinforcing material and their contribution to producing a fiber-reinforced pipe having a high glass content. Preferred phenolic novolacs found most useful in this invention are prepared from any of the phenols and aldehydes previously described

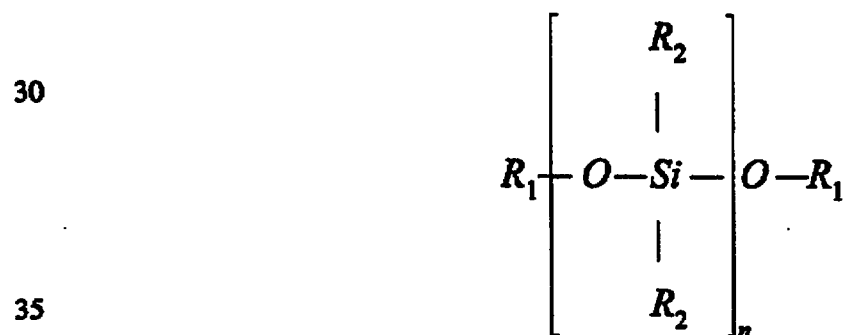
1 and have molecular weights in the range of from about 400 to 5,000 with glass transition
temperatures in the range of from about 40°C to 90°C. Phenolic resoles found most useful
in this invention have molecular weights in the range of from about 300 to 3,000, solids
contents from 50 to 90% by weight, and may contain from 2 to 20% by weight free phenol
5 or substituted phenol and from 1 to 10% by weight water.

Manufacturers of suitable phenolic resins include: B.P. Chemical Division of British
Petroleum of Barry U.K.; the Packaging and Industrial Products Division of Borden, Inc.,
of Columbus, Ohio; the Durez Division of Occidental Petroleum of Dallas, Texas;
Georgia-Pacific Corporation of Atlanta, Georgia; Neste Resins Corporation of Eugene,
10 Oregon, as well as a number of other small producers. Some preferred phenolic resins
include B.P. Chemical's Cellobond J1996L, J2018L and J2027L, Borden's SL-898 phenolic
resole, and Georgia-Pacific's GP5018 phenolic resole.

Particularly preferred siloxane-modified phenolic resins useful in forming the structural
pipe wall include those prepared by combining, in a first embodiment, a silicone
15 intermediate, a phenol or substituted phenol, and an aldehyde donor, by combining, in a
second embodiment, one of the above-described phenolic novolac resins with a silicone
intermediate, or by combining, in a third embodiment one of the above-described phenolic
resole resins with a silicone intermediate.

In a first embodiment, a siloxane-modified phenolic resin is prepared by combining
20 phenol or a substituted phenol described above, with an aldehyde described above, and a
silicone intermediate. The amount of aldehyde present and the type of catalyst used will
determine whether a siloxane-modified phenolic novolac or resole resin is formed.

With respect to the silicone intermediate, alkoxy-functional and silanol-functional
silicone intermediates may be used. Silicone intermediates as referred to in this invention
25 are chemical polymer structures that have an -Si-O- backbone and that are capable of
undergoing further reaction, e.g., hydrolysis and/or condensation, to form a cured polymer
structure. A preferred class of silicone intermediates have the formula



1 where each R_2 is independently selected from the group consisting of the hydroxy group,
alkyl, aryl, aryloxy, and alkoxy groups having up to six carbon atoms, where each R_1 is
independently selected from the group consisting of hydrogen, alkyl, and aryl groups having
5 up to 12 carbon atoms, and where n is an integer in the range of from 1 to 56, selected so
that the average molecular weight of the silicone intermediate is from about 150 to about
10,000. It is believed that the molecular weight of the silicone intermediate selected may
have an impact on the degree to which an interpenetrating network (IPN) of phenolic polymer
and siloxane polymer is formed, and the proportion of siloxane groups that copolymerize
with the phenolic polymer to form a continuous phase.

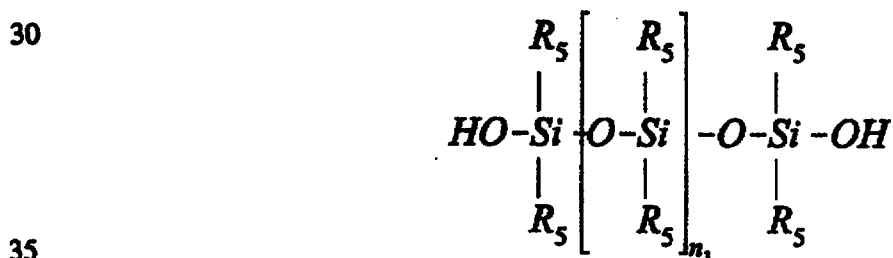
10 Another group of silicone intermediate can be represented by an hydroxyl (OH)
containing silicone material, including those materials wherein the OH group or groups are
attached directly to the silicon atom such as the silanol materials having the general formulas



20 and

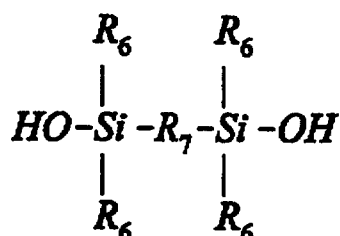


and



where each R_5 group may comprise a hydrocarbon radical selected from the group
including alkyl, alkenyl, cycloalkyl, aryl, alkaryl, or aralkyl radicals, and where n_1 may be
an integer in the range of from about one to thirty.

1 Still another group of OH containing silicone materials are materials that comprise two or more OH groups attached to a silicon atom, and that have two or more silicon atoms attached through divalent organic radicals, such as those having the general formula



5 where each R_6 group may comprise another OH group or may comprise a hydrocarbon radical selected from the group including alkyl, cycloalkyl, aryl, alkaryl, and alkylaryl radicals, where R_7 may comprise a divalent organic radical selected from the group including methylene, polymethylene, arylene, polyarylene, cycloalkylene, and polycycloalkylene.

15 Methoxy-functional silicone intermediates useful in this invention include, but are not limited to: DC-3074, DC-3037 from Dow Corning Corporation of Midland, Michigan; SY-231 (molecular weight approximately 1,000) and MSE-100 from Wacker Silicone Corporation; and SR-191 from General Electric. Silanol-functional silicone intermediates generally have in the range of from about 0.5% to 6% by weight Si-OH. Commercially available silanol-functional silicone intermediates useful in this invention include, but are not limited to: Diphenylsilandiol (molecular weight approximately 216), Wacker Silicones SY-409 (molecular weight approximately 10,000) and SY-430; and the following materials from Dow Corning: DC804, DC805, DC806A, DC840, Z-6018, DC-1-2530, DC-6-2230, DC-1-0409, DC-1-0410 and laminating resins 2103, 2104 and 2106.

25 A preferred first embodiment of a siloxane-modified phenolic resin is prepared by combining phenol, or substituted phenol, an aldehyde such as formaldehyde, and a silicone intermediate. On the basis of a charge weight of one mole of phenol, the weight of formaldehyde will vary between 0.75 and 0.90 moles, and the weight of silicone intermediate will vary between 0.01 and 0.3 moles. The molar ratio of phenol to formaldehyde in a phenolic novolac resin is typically 1:0.75-0.90. Table 1 shows the typical molar ranges of silicone intermediates, having different molecular weights, used to prepare the siloxane-modified phenolic novolac resin.

TABLE 1

SILICONE INTERMEDIATE	MOLECULAR WEIGHT	1 MOLE PHENOL AND 0.75 MOLE FORMALDEHYDE	1 MOLE PHENOL AND 0.90 MOLE FORMALDEHYDE
Diphenylsilandiol	216	0.01-0.3 mole silicone intermediate	0.01-0.3 mole silicone intermediate
SY-231	1,000	0.01-0.2 mole silicone intermediate	0.01-0.2 mole silicone intermediate
SY-409	10,000	0.01-0.05 mole silicone intermediate	0.01-0.05 mole silicone intermediate

A first preferred embodiment of a siloxane-modified phenolic resole resin is prepared by combining phenol, or substituted phenol, an aldehyde such as formaldehyde, and a silicone intermediate. On the basis of a charge weight of one mole of phenol, the weight of formaldehyde will vary between 1.2 and 3 moles, and the weight of silicone intermediate will vary between 0.01 and 0.7 moles. The molar ratio of phenol to formaldehyde in a phenolic resole resin is typically 1:1.2-3. Table 2 shows the typical ranges of silicone intermediates having different molecular weights used to prepare the siloxane-modified phenolic resole resin.

TABLE 2

SILICONE INTERMEDIATE	MOLECULAR WEIGHT	1 MOLE PHENOL 1.2 MOLE FORMALDEHYDE	1 MOLE PHENOL 3 MOLE FORMALDEHYDE
Diphenylsilandiol	216	0.01-0.7 mole silicone intermediate	0.01-0.3 mole silicone intermediate
SY-231	1,000	0.01-0.02 mole silicone intermediate	0.01-0.02 mole silicone intermediate
SY-409	10,000	0.01-0.05 mole silicone intermediate	0.01-0.05 mole silicone intermediate

For each of the above-described first embodiments of the siloxane-modified phenolic novolac and resole resins, it is desired that in the range of from about 0.5 to 35 percent by weight of the silicone intermediate be used.

In preparing first embodiments of the siloxane-modified phenolic resins, catalysts are used to form either a desired phenolic novolac or phenolic resole resin prepolymer. For example, when forming the siloxane-modified phenolic resin, a strong acid such as sulfuric acid, sulfonic acid, oxalic acid, or phosphoric acid is used to facilitate formation of the phenolic novolac resin prepolymer. When forming the siloxane-modified phenolic resin, a strong base such as sodium hydroxide, calcium hydroxide or barium hydroxide is used to facilitate formation of the phenolic resole prepolymer. In preferred first embodiments, a siloxane-modified phenolic novolac resin may be prepared by using up to about five percent by weight acid catalyst, and a siloxane-modified phenolic resole resin may be prepared by using up about five percent by weight base catalyst.

Catalysts other than, and in addition to, those described above can optionally be used in preparing first embodiments of the siloxane-modified phenolic resin to facilitate condensation of the phenolic resin and silicone intermediate by reducing the time and/or temperature associated with such reactions. Catalysts useful for facilitating condensation of the phenolic resin and silicone intermediate are the same, and can be used in the same proportion, as those described below that can optionally be used for preparing second and third embodiments of the siloxane-modified phenolic resin.

First embodiments of the siloxane-modified phenolic novolac and resole resins are prepared by first combining the phenol and silicone intermediate ingredients and then adding the aldehyde ingredient to form a mixture of phenolic polymers, siloxane polymers, and

1 phenolic-siloxane polymers. Elevating the temperature of the combined mixture is desirable to reduce reaction times associated with forming the siloxane-modified phenolic resin.

For example, a first embodiment of the siloxane-modified phenolic novolac resin can be prepared by a batch process using a jacketed stainless-steel reaction vessel equipped with
5 a turbine blade or anchor-type agitator, a vapor condenser, and a temperature controller. Typically, molten phenol is charged to the reaction vessel, the agitator is started and silicone intermediate is added. An acid catalyst can be added at this point to facilitate formation of the phenolic novolac polymer. Formalin (37-40 percent aqueous formaldehyde) is then charged to the reaction vessel, either before raising the temperature, or by controlled addition
10 at elevated temperature. A vigorous condensation reaction ensues which is highly exothermic. The condensation step is continued until the desired molecular weight distribution has been achieved. During this time the mixture may become two phases with separation of the resinous component. The actual reaction time will vary depending on the desired molecular weight distribution, the use of one or more catalysts, pH, and aldehyde to phenol to silicone intermediate mole ratios.

The ingredients are mixed together, during which time the phenol, aldehyde and silicone intermediate undergo polycondensation, which polycondensation can optionally be accelerated by action of a catalyst, as described below. During this time, alkoxy-functional
- silicone intermediates also undergo hydrolysis to form silanol-functional silicone
20 intermediates, which polymerize to form a siloxane polymer and also copolymerize with the newly-formed phenolic novolac resin prepolymer to form a siloxane-modified phenolic resin. Accordingly, the resulting resin comprises an IPN of phenolic novolac polymer and siloxane polymer, and a continuous phase formed from the phenolic polymer having one or more siloxane groups in its backbone. Hydrolysis of the alkoxy-functional silicone intermediates
25 can optionally be accelerated by action of a catalyst, as described below. Alternatively, silanol-functional silicone intermediates can be used in the process which can copolymerize directly with newly-formed phenolic novolac resin prepolymer.

At the end of the condensation period, water, residual moisture, unreacted phenol and low molecular weight species may be removed by atmospheric, vacuum or steam distillation.
30 The point at which distillation is stopped is usually determined by taking a sample of the resin and measuring its melt viscosity. After the resin has cooled, it can be treated in several ways. It can be sold in lump or flake form, compounded to form molding powders, or it can be ground and blended with hexamine and other fillers.

As another example, a first embodiment of the siloxane-modified phenolic resole resin
35 can be prepared by a batch process using the same equipment previously described for preparing a first embodiment of the siloxane-modified phenolic novolac resin. Typically, molten phenol is charged to the reaction vessel, the agitator is started and silicone intermediate is added. Alkaline catalysts may be added at this time to facilitate formation

1 of the phenolic resole polymer. Formalin is added and the batch is heated. The initial
reaction is exothermic. Condensation is usually carried out at atmospheric pressure and at
temperatures in the range of from 60 to 100°C or at reflux. Because siloxane-modified
phenolic resole siloxane resins are themselves thermosetting, dehydration is carried out
5 quickly and at low temperatures so as to prevent over-reaction or gelation. The end point
is found by manual determination of a specific hot-plate gel time, which decreases as
resinification advances. Siloxane-modified phenolic resole resins can be refrigerated to
prolong their storage stability.

Second and third embodiments of a siloxane-modified phenolic novolac resin and a
10 siloxane-modified phenolic resole resin, respectively, are prepared by using a phenolic
novolac resin and phenolic resole resin, respectively, as starting materials. Suitable phenolic
resole and phenolic novolac resins include those previously described above. The second
embodiment of the siloxane-modified phenolic novolac resin is prepared by combining in the
range of from 75 to 95 percent by weight of the phenolic novolac resin. The third
15 embodiment of the siloxane-modified phenolic resole resin is prepared by combining in the
range of from 65 to 99.5 percent by weight of the phenolic resole resin.

With respect to the silicone intermediate, those silicone intermediates previously
described for preparing the first embodiments of the siloxane-modified phenolic resin are also
used to prepare the second and third embodiments of the siloxane-modified phenolic resins.
20 Second and third embodiments of the siloxane-modified phenolic resins may each comprise
in the range of from 0.5 to 35 percent by weight of the alkoxy-functional or silanol-functional
silicone intermediate.

In the second embodiment, the siloxane-modified phenolic novolac resin is prepared
by combining a phenolic novolac resin with a formaldehyde donor and a silicone
25 intermediate. Suitable formaldehyde donors include aqueous formaldehyde solutions,
paraform, trioxane, hexamethylenetetraamine and the like, a preferred material is
hexamethylenetetraamine. The second embodiment of the siloxane-modified phenolic novolac
resin may comprise in the range of from about 3 to 15 percent by weight of the formaldehyde
donor.

30 The third embodiment of a siloxane-modified phenolic resole resin is prepared by
combining a phenolic resole resin with a silicone intermediate. If desired, either an acid or
base catalyst can optionally be used to reduce reaction time associated with finally curing the
resin. Suitable inorganic acid catalysts that can optionally be used in the third embodiment
include phosphoric, hydrochloric, and sulfuric acids. Suitable organic acids that can
35 optionally be used in the third embodiment include paratoluene sulfonic and phenyl sulfonic
acids. Latent acid catalysts can also be used in to improve pot life and to increase the
application window without gel formation. Suitable base catalysts for curing phenolic resoles
include various forms of barium and magnesium oxide, and the like. Commercially available

1 proprietary latent acid type catalysts useful in this invention are available from British
 Petroleum Chemicals under the trade name Phencat 381 and Phencat 382. Other proprietary
 catalysts include Borden RC-901, a diphenyl phosphoric acid ester supplied from Dover
 Corp., having the product name Doverphos 231L, and Georgia-Pacific's GP3839 and
 5 GP308D50. The third embodiment of the siloxane-modified phenolic resole resin may
 comprise up to about 15 percent by weight of the optional acid or base catalyst or curing
 agent.

10 If desired, the first, second and third embodiments of the siloxane-modified phenolic
 resins may each optionally comprise a sufficient amount of catalyst to reduce the reaction
 time and reduce the reaction temperatures associated with condensing the silicone
 intermediate and copolymerizing it with the phenolic polymer during formation of the
 siloxane-modified phenolic resin.

15 Suitable catalysts are selected from the group consisting of organometallic compounds,
 amine compounds, and mixtures thereof. Combinations of an organometallic compound with
 an amine compound are preferred, when desired, for catalyzing hydrolysis and/or
 condensation of the silicone intermediate. Useful organometallic compounds include metal
 driers well known in the paint industry such as zinc, manganese, cobalt, iron, lead and tin
 octoate, neodecanates and naphthenates, and the like. Organotitanates such as butyl titanate
 and the like are also useful in the current invention.

20 A preferred class of organometallic compounds useful as a catalyst is organotin
 compounds which have the general formula

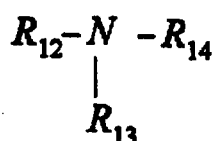


30 where R_8 , R_9 , R_{10} and R_{11} are selected from the group consisting of alkyl, aryl, aryloxy,
 and alkoxy groups having up to 11 carbon atoms, and where any two of R_8 , R_9 , R_{10} and
 R_{11} are additionally selected from a group consisting of inorganic atoms consisting of
 halogen, sulfur and oxygen.

35 Organotin compounds useful as catalysts include tetramethyltin, tetrabutyltin,
 tetraoctyltin, tributyltin chloride, tributyltin methacrylate, dibutyltin dichloride, dibutyltin
 oxide, dibutyltin sulfide, dibutyltin acetate, dibutyltin dilaurate, dibutyltin maleate polymer,
 dibutyltin dilaurylmercaptide, tin octoate, dibutyltin bis (isooctylthioglycolate), butyltin
 trichloride, butylstannic acid, dioctyltin dichloride, dioctyltin oxide, dioctyltin dilaurate,
 dioctyltin oxide, dioctyltin dilaurate, dioctyltin maleate polymer, dioctyltin bis

(isooctylthioglycolate), dioctyltin sulfide, and dibutyltin 3-mercapto propionate. The first, second and third embodiments of the siloxane-modified phenolic resin may comprise up to about five percent by weight of the organometallic catalyst.

With respect to the amine compound, preferred amine compounds for optionally catalyzing the hydrolysis and/or condensation reactions of the silicone intermediate have the general formula



where R_{12} and R_{13} are each selected from the group consisting of hydrogen, aryl, and alkyl groups having up to 12 carbon atoms, and where R_{14} is selected from the group consisting of alkyl, aryl, and hydroxyalkyl groups having up to 12 carbon atoms.

Suitable amine compounds useful as catalysts include dimethyl methanolamine, ethylamino ethanol, dimethyl ethanolamine, dimethyl propanolamine, dimethyl butanolamine, dimethyl pentanolamine, dimethyl hexanolamine, methylethyl methanolamine, methylpropyl methanolamine, methylethyl ethanolamine, methylethyl propanolamine, monoisopropanolamine, methyldiethanolamine, triethanolamine, diethanolamine, and ethanolamine. Preferred amine compounds include dimethyl ethanolamine and ethyl aminoethanol. The first, second and third embodiments of the siloxane-modified phenolic resin may comprise up to about five percent by weight of the amine catalyst.

If desired, the organometallic compound and amine compound can each be used independently to form a siloxane-modified phenolic resin. However, it has been discovered that when combined, the organometallic compound and amine compound act synergistically to catalyze the curing process, thereby reducing the curing time further and/or reaction temperatures greater than that observed by using either the organometallic or amine catalyst alone. Accordingly, if desired under the circumstances, it is preferred that an organometallic compound be used in combination with an amine compound to catalyze both the formation of hydroxide by hydrolysis of the silicone intermediate, in the event that an alkoxy-functional silicone intermediate is used, and polymerization by condensation of both the alkoxy and silanol-functional silicone intermediate. An exemplary organometallic and amine compound combination is dibutyltin diacetate and ethyl aminoethanol. Dibutyltin diacetate, when combined with the amine, reacts synergistically to catalyze the curing process. Although it is believed that the synergistic effect of the organotin compound and the amine compound is mechanistic in character, the exact mechanism is not known.

1 A preferred ratio of organometallic compound to amine compound, when used together
as the catalyst, is approximately one to one. Therefore, the first, second and third siloxane-
modified phenolic resins may comprise up to about 10 percent by weight combined
organometallic and amine catalyst. Accordingly, siloxane-modified phenolic resins prepared
5 by combining an organometallic and amine catalyst, and an optional acid or base catalyst may
comprise up to about 25 percent by weight catalyst. Preferred first, second and third
siloxane-modified phenolic resins comprise in the range of from 5 to 25 percent by weight
of the combined catalysts.

10 Water may be present in the form of an aqueous phenolic resole or in the form of an
aqueous formaldehyde. For example, the phenolic resole may comprise in the range of from
3 to 12 percent by weight water, and the formaldehyde may comprise formalin, which is
approximately 37-40 percent aqueous formaldehyde. The first, second and third
embodiments of the siloxane-modified phenolic resin can result in the formation of phenolic
resins having very low or zero water content, which provides improved fire stability and
15 processing characteristics. The silicone intermediate functions as a reactive diluent to give
a stable product with generally low viscosity.

20 Second and third embodiments of the siloxane-modified phenolic resin are prepared
by combining in the above-described proportions a phenolic novolac or resole resin with a
methoxy or silanol-functional silicone intermediate. A formaldehyde donor is added in the
second embodiment. If desired, the catalyst for the phenolic resin, and the catalyst for the
silicone intermediate, i.e., the organometallic compound and/or the amine compound, can
optionally be added to reduce reaction and cure time and reduce reaction temperature.

25 Fire resistant pipes having the structural pipe wall and fire resistant layer formed from
siloxane-modified phenolic resins display improved physical properties of hoop strength,
chemical resistance, flexibility, impact resistance, and flexural modulus when compared to
pipes otherwise formed from non-modified phenolic resins, without affecting the physical
properties of heat, flame and chemical resistance inherent in the phenolic resin.
Additionally, fire resistant pipes formed from such siloxane-modified phenolic resins have
reduced microvoid formation and, therefore, densities closer to theoretical density when
30 compared to conventional non-modified phenolic resins. Less microvoid formation also
prevents possible water entrapment that would adversely affect the resin's temperature
resistant properties due to steam generation and related resin matrix failure.

35 Furan resins can be selected for use in forming the structural pipe wall because of their
enhanced temperature resistance when compared with conventional epoxy and polyester FRP
resins. Furan resins, however, display a lower degree of temperature resistance and are
more expensive than either the phenolic or siloxane-modified phenolic resins.

 The structural pipe wall of the fire resistant pipe is constructed having one or more
layers of fiber windings. For example, for an approximately two inch inside diameter pipe,

1 rated at 225 psig for fire fighting pipe service, it is desired that the structural wall comprise
in the range of from 2 to 20 layers of fiber winding, and optimally 6 to 16 layers of fiber
winding. A structural pipe wall having less than about 2 layers of fiber winding will have
5 a degree of hoop and longitudinal strength, and temperature resistance less than that desired
for use in a fire fighting pipe application. A structural pipe wall constructed having more
than about 20 layers of fiber winding is more than that necessary to provide a sufficient
degree of hoop and longitudinal strength, and temperature resistance for use in a fire fighting
pipe application and, therefore adds unnecessary weight and expense to the pipe.

Referring now to FIG. 2, in a first embodiment, a fire resistant layer 18 is disposed
10 around the outside surface of the structural pipe wall 12. The fire resistant layer 18 is
generally a resin rich heat-ablative shield that is used to surround the structural pipe wall 12
and protect it from exposure to high temperature or direct flame contact. The fire resistant
layer 18 comprises a carrier component 20 that is impregnated with a resin component 22.
Typically, fire resistant layer 18 is wound circumferentially around the outside surface of the
15 structural pipe wall 12 until a desired number of layers, i.e., heat shield wall thickness, is
obtained. The fire resistant layer can, however, be applied by a spray application technique.

FIG. 3 illustrates a first embodiment of a fire resistant pipe 10 constructed according
to principles of this invention comprising a structural wall 12 formed from multiple fiber
windings 14, and multiple fire resistant layers 18. The number of fire resistant layers that
20 are used to form the fire resistant pipe or pipe fitting varies, depending such factors as the
size of the pipe, the potential temperature or flame exposure by the pipe, the type of fiber
and/or resin component selected to form the structural pipe wall, the type of carrier and/or
resin component selected to form the fire resistant layer, and the like. Preferred
embodiments of the first fire resistant pipe embodiment may include in the range of from 1
25 to 15 fire resistant layers, depending on the above-mentioned factors. In one example, for
an approximately two inch inside diameter pipe, the fire resistant pipe comprises in the range
of from 2 to 15 fire resistant layers.

The fire resistant layer 18 can be wound around the structural pipe wall 12 by
conventional winding techniques, such as those described above for constructing the structural
30 pipe wall. It is desired that the fire resistant layer be wound at a sufficient tension to provide
a good interface between the adjoining pipe wall and fire resistant layer surfaces. In a
preferred first embodiment, the fire resistant layer 18 is applied shortly after forming the
structural pipe wall, and before the resin component of the pipe wall has cured, to provide
good interlayer bonding during cure between the interfacing resin components of the pipe
35 wall and fire resistant layer. Accordingly, as described below, it is desired that the resin
component of the fire resistant layer be compatible with the resin used to form the structural
pipe wall.

1 The carrier component 20 used to form the fire resistant layer 18 can be formed from
any type of material capable of both accommodating a large amount of the resin component
and providing a support structure for the resin in both a wet and cured state. Additionally,
5 it is desired that the carrier be capable of supporting the resin and not crumbling or flaking
away from the structural pipe wall when subjected to high temperature or direct flame. It
is desired that the carrier be capable of accommodating in the range of from 75 to 95 percent
by weight of the resin component, or roughly three times the resin content of the fiber-
reinforced windings. In a preferred first embodiment, the fire resistant layer comprises
approximately 90 percent by weight resin.

10 Suitable carrier materials include fibrous mat-like structures comprising glass fiber,
carbon fiber, mixtures of polyester fiber or nylon fibers with other high-temperature fibers,
similar fiber felts, chopped fibers, and the like, and combinations thereof. A preferred glass
fiber containing carrier material is one manufactured by Owens Corning of Toledo, Ohio
under the product name C-Veil, product code number GC 70E, which is a thin mat of
15 randomly oriented chopped C-glass fibers that are bound together by a binder dispersion.
A preferred polyester fiber containing material is one manufactured by Precision Fabrics
Group of Greensboro, North Carolina under the product name Nexus, product code number
111-00005, which is formed from stretched and heat set 100 Dacron® polyester, and that
does not contain any glass fibers.

20 Although the carrier component has been described and illustrated as being a mat-like
structure applied by conventional winding technique, it is to be understood that the carrier
can alternatively be in the form of a spray applicable material containing chopped fibers and
resin. Suitable spray applicable carriers include those capable of being loaded with the
above-described amount of the resin component for spray application onto the surface of the
25 structural pipe wall using conventional spray application techniques.

 The carrier component provides a fibrous reinforcement in the resin matrix of the fire
resistant layer. The fibers provide mechanical strength for the resin which may be somewhat
brittle. Thermal decomposition of the resin makes it brittle even when relatively impact
resistant before exposure. The effect is that the fire resistant layer at most ablates in fine
30 particles instead of spalling in large flakes that would rapidly deplete the resin rich protective
layer and expose the underlying structural wall of the pipe to thermal degradation.
Surprisingly, some thermoplastic resin fibers may be used even though they would seem to
be subject to significant degradation in a flame test. Such fibers work best, however, when
mixed with high-temperature fibers. Glass fibers are, however, preferred for strength and
35 temperature resistance.

 The resin component 22 used to impregnate the carrier component to form the fire
resistant layer 18 is selected from the same group of phenolic resins, siloxane-modified
phenolic resins, furan resins, and mixtures thereof described above for the resin used to form

1 the structural pipe wall. The resin component is applied to the carrier, when embodied as
a mat-like structure, by the same technique described above for applying resin to the fiber-
reinforced windings. It is preferred that the resin component selected for the fire resistant
5 layer be the same as that selected to form the underlying structural pipe wall to ensure
chemical compatibility and, thereby provide a good chemical bond between interfacing
structural pipe wall and fire resistant layer surfaces during cure. Furthermore, by using the
same resin, a single cure cycle is used for the entire pipe.

The first fire resistant pipe embodiment may be constructed having one or more
layer(s) of the same type of fire resistant material, or may be constructed having one or more
10 layers of different types of the fire resistant material. It is desired that the resin component
of each different type of fire resistant material be compatible with the resin component of the
adjacent structural pipe wall or fire resistant layer surface to promote good interlayer
bonding. For example, the fire resistant pipe or pipe fitting may include, moving outwardly
from the surface of the pipe wall, one or more layer(s) of the C-Veil-type material, one or
15 more layer(s) of the Nexus type material, and one or more layer(s) of the C-Veil type
material, each impregnated with the same resin component as that used to form the structural
pipe wall. The use of different types of fire resistant layers may be desired to reduce raw
material costs, optimize temperature resistance, minimize weight, or the like. In a preferred
first fire resistant pipe embodiment, the fire resistant layer is formed from alternating layers
20 of C-glass fiber (C-Veil) and polyester material (Nexus) impregnated with a siloxane-
modified phenolic resin composition.

After the structural pipe wall has been formed, and the fiber resistant layer has been
applied, the resin components of the first fire resistant pipe embodiment are cured
simultaneously by exposing the pipe to a temperature in the range of from about 140 to
25 190°F (60 to 88°C) for a period of about 30 minutes. It is desired that the resins used to
form the structural pipe wall and the fire resistant pipe comprise sufficient catalyst to effect
cure at a temperature below about 212°F (100°C). It is to be understood that the cure
conditions for the pipe may vary depending on the amount and/or type of catalyst used, the
type of resin selected, the number of fiber-reinforced windings, the number of fire resistant
30 layers, and the like.

The cured fire resistant layer acts as a heat ablative coating that forms a porous outer
layer when exposed to conditions of high-temperature or direct flame. The porous outer
layer does ablate away from the pipe but, remains intact to form a heat insulating layer that
protects the underlying structural pipe wall from potentially damaging effects of such high-
35 temperature or direct flame conditions.

Referring now to FIG. 4, a second fire resistant pipe embodiment constructed
according to principles of this invention includes a structural wall 24, constructed as
described above for the first fire resistant pipe embodiment, and one or more layers of an

1 energy absorbing material 26 disposed onto the surface of the structural pipe wall. The
energy absorbing material used to form the layer is preferably one capable of absorbing a
large degree of heat from an outside surrounding layer and using such energy, e.g., via an
5 endothermic reaction, to effect a phase change, e.g., from solid to gas, below the degradation
temperature of the structural wall. The gas formed from the layers produce a thermally
insulating air gap between the outside surrounding layer and the structural pipe wall.

Suitable energy absorbing materials include polymeric materials, solid hydrate or
hydrite materials and the like that are capable of undergoing an endothermic phase
transformation to vaporize, or liberate a gas, at a temperature below the degradation
10 temperature of the resin selected to form the underlying structural wall, i.e., below about
300°C. Examples of preferred energy absorbing materials include polyethylene, hydrated
calcium sulfate (gypsum), aluminum trihydroxide, and other hydrated or hydroxide containing
compounds capable of vaporizing or producing a gas constituent below about 300°C.
Polymeric materials, such as polyethylene and the like, filled with a powder component are
15 also desired, as the combination of gas and powder produced during vaporization produces
a gas and powder layer between the outside surrounding layer and the structural pipe wall
having enhanced thermal insulating properties.

When polyethylene is used as the energy absorbing material to form a second fire
resistant pipe embodiment, it can be wound in sheet form around the structural pipe wall 24
20 a number of times to form a desired number of layers or layer thickness. When polyethylene
in the form of 0.15 millimeter thick sheet is used, it is desired that in the range of from 4
to 20 layers be used, thereby providing a total energy absorbing material wall thickness in
the range of from about 0.6 to 3 millimeters. The polyethylene sheet is applied by the same
winding technique described above for the structural pipe wall and fire resistant layer of the
25 first fire resistant pipe embodiment. It is not necessary that the polyethylene layer be applied
at a specific wind angle, since it is intended to be sacrificial and not contribute to the hoop
or longitudinal strength of the pipe. Where the energy absorbing material is other than
polyethylene, it can be applied in sheet form, in spray form, or in the form of solid half
sheets configured to fit over part of the structural pipe wall.

30 Layers of fiber-reinforced resin 28 are wound around an outside surface of the energy
absorbing material layer 26. The fiber-reinforced resin can be the same as that selected to
form the structural pipe wall 24, or can be different. In a preferred second fire resistant pipe
embodiment, the fiber-reinforced resin is the same, and is applied in the same manner, as
that selected to form the structural pipe wall. The number of layers of the fiber-reinforced
35 resin that is applied depends on the particular pipe application and the degree of heat or
flame resistance desired. Preferred second fire resistant pipe embodiments may include in
the range of from 2 to 20 layers of the fiber-reinforced resin 28.

1 Alternatively, a second fire resistant pipe embodiment may comprise a number of
repeating fiber-reinforced resin layers and energy absorbing material layers. For example,
a fire resistant pipe can include first energy absorbing material layers disposed onto the
structural pipe wall, first fiber-reinforced resin layers disposed onto an outside surface of the
5 first energy absorbing material layers, second energy absorbing layers disposed onto a
surface of the first fiber-reinforced resin layers, and second fiber-reinforced resin layers
disposed onto an outside surface of the second energy absorbing material layers. In such an
embodiment, the energy absorbing materials selected to form the first and second energy
absorbing material layers can be the same or can be different, and can be selected so that an
10 energy absorbing material having a relatively higher vaporization temperature below the
degradation temperature of the fiber-reinforced resin layers is used to form the outermost
energy absorbing material layer. In such an embodiment, the number of each energy
absorbing material layers can be the same as or less than that disclosed above for an
embodiment having a single energy absorbing material layer.

15 Referring to FIG. 5, an alternative second fire resistant pipe embodiment can include
two different types of energy absorbing material layers positioned adjacent one another to
provide a desired degree of energy absorption and thermal insulation. For example, a
number of first energy absorbing material layers 30, of a first type of energy absorbing
material, are disposed onto a surface of the structural pipe wall 32. A number of second
20 energy absorbing material layers 34, of a second type of energy absorbing material, are
disposed onto a surface of the first energy absorbing material layers. Preferably, the second
type of energy absorbing material has a relatively higher vaporization temperature than the
first type of energy absorbing material so that the two layers act as a sequential thermal
insulator to prevent harmful heat energy from reaching the structural pipe wall.

25 A number of fiber-reinforced resin layers 36 are wound around an outside surface of
the second energy absorbing material layer. The number of fiber-reinforced resin layers 36
that are used can be the same as or less than that used to form the structural pipe wall.
Additionally, the type of fiber reinforcing material and resin used to form the fiber-reinforced
resin layer 36 can be the same as or different than that used to form the structural pipe wall.
30 The number of energy absorbing material layers used to form the first and second energy
absorbing material layer can be the same as or different than that used to form the single
energy absorbing material layer embodiment disclosed above.

 If desired, the second alternative fire resistant pipe embodiment can be formed having
more than one set of energy absorbing material layers to provide a desired degree of heat
35 and/or flame protection to the structural pipe wall. For example, the fire resistant pipe can
be formed having a structural pipe wall, a first set of different energy absorbing material
layers, a first fiber-reinforced resin layer, a second set of different energy absorbing material
layers, and a second fiber-reinforced resin layer. In such embodiment, the types of energy

1 absorbing materials that are used to form the first set of energy absorbing material layers can be the same as or different than that used to form the second set of energy absorbing material layers.

5 Alternatively, the first fire resistant pipe embodiment can be constructed having one or more layers of an energy absorbing material described above interposed between the structural pipe wall and the fire resistant layers to provide an enhanced degree of heat or flame protection to the structural pipe wall. In such an embodiment, the resin component used to form the heat shield can be different than the resin component used to form the structural pipe wall.

10 Additionally, if desired, the first fire resistant pipe embodiment can be constructed having one or more energy absorbing layers interposed between different types of fire resistant layers. Accordingly, it is to be understood within the scope of this invention that one or more energy absorbing material layers can be placed between the structural pipe wall and fire resistant layers and/or between different types of fire resistant layers as desired, depending on the particular application, to provide an optimum degree of heat and flame protection to the structural pipe wall.

15 Referring now to FIG. 6, a third embodiment fire resistant pipe 38 constructed according to principles of this invention includes a release layer 40 disposed onto an outside surface of the structural pipe wall 42, and a fiber-reinforced resin layer 44 disposed onto a surface of the release layer 40. In such third embodiment, the structural pipe wall is formed in the same manner previously described for the first and second fire resistant pipe embodiments. In an exemplary embodiment, the third embodiment fire resistant pipe comprises a jacket 46 of alternating release layers 40 and fiber-reinforced resin layers 44 disposed around the outside surface of the structural pipe wall 42.

20 Materials useful for forming the release layer 40 are preferably those that neither bond with the resin used to form the adjacent structural pipe wall or with the resin used to form the fiber-reinforced resin layer. It is desired that the release layer not form a bond with an adjacent structural pipe wall or fiber-reinforced resin wall to permit the release layer to act as a disbondment layer between the resin-containing layers. The disbonding action of the release layer serves to improve the impact of the fire resistant pipe by attenuating the travel of any shock waves through the pipe caused by contact made to the outside surface. Functioning in this manner, the release layers act to deaden or prevent potentially damaging impact shock waves from traveling completely through the pipe to the structural wall, thereby preventing possible fracture or rupture.

25 Suitable materials for forming the release layers include films formed from polymeric materials that are chemically incompatible with the particular resin used to form the structural pipe wall and fiber-reinforced resin layers. Examples of such polymeric materials include

1 polyolefins such as polypropylene, polyethylene and the like. A particularly preferred release layer is formed from polypropylene.

It is also desired that the material selected to form the release layer be capable of absorbing heat energy applied from the pipe surface, and preferably be a material capable of absorbing a large degree of heat from an outside surrounding layer and using such energy, e.g., via an endothermic reaction, to effect a phase change, e.g., from solid to gas, below the degradation temperature of the structural wall. The gas formed from the release layer(s) acts to form a thermally insulating air gap between the adjacent fiber-reinforced resin layer, and between the fiber reinforcing layers and the structural pipe wall. The air gap allows each of the independent fiber-reinforced resin layers to act as a radiation shield to increase the thermal resistance of the pipe by requiring that radiant heat be progressively transferred through each fiber-reinforced resin layer before reaching the structural pipe wall. The multi-radiation shield function of the air gaps avoids the potentially high wall stresses in the pipe caused by the steep thermal gradient on the outside of the pipe during a fire.

15 The materials noted above for forming the release layers are also heat absorbing and, therefore, useful in forming a release layer that is both disbonding and energy absorbing. Other suitable release layer materials include solid hydrate or hydrite materials and the like, as discussed above for forming the layers of energy absorbing materials, that are capable of undergoing an endothermic phase transformation to vaporize, or liberate a gas, at a temperature below the degradation temperature of the resin selected to form the underlying structural wall, i.e., below about 300°C. Examples of preferred energy absorbing materials include polypropylene, polyethylene, hydrated calcium sulfate (gypsum), aluminum trihydroxide, and other hydrated or hydroxide containing compounds capable of vaporizing or producing a gas constituent below about 300°C.

25 Polymeric materials, such as polypropylene, polyethylene and the like, filled with a powder component are also desired, as the combination of gas and powder produced during vaporization produces a gas and powder layer between the outside surrounding layer and the structural pipe wall having enhanced thermal insulating properties.

The number of alternating release and fiber-reinforced resin layers used to form the jacket that surrounds the structural pipe wall depends on the particular fire pipe application and the degree of heat or flame resistance desired. In an exemplary embodiment, for a pipe having a structural pipe wall diameter of approximately two inches (51 millimeters), a minimum jacket thickness is approximately 1/8 inches (3 millimeters) comprising four each alternating release and fiber-reinforced resin layers, as shown in FIG. 6. In forming pipe fittings, such as elbows, Y-connections, T-connections and the like, a minimum jacket thickness of approximately 1/8 inches (3 millimeters) is desired. It is to be understood that the exact number of release and fiber-reinforced resin layers that are used to make up a

1 jacket of any designated thickness depends on the thickness of both the release layer material and the fiber-reinforcing material.

When the release layer of the jacket is polypropylene tape, it is applied to the structural pipe wall by the same winding technique described above for the structural pipe wall. Where the release layer is other than polypropylene or other material in tape form, it can be applied in sheet form, in spray form, or in the form of solid half sheets configured to fit over part of the structural pipe wall.

Each fiber-reinforced resin layer is wound around an outside surface of a respective release layer. The material use to form the fiber-reinforced resin layers can be the same as that selected to form the structural pipe wall, or can be different. In a preferred embodiment, the fiber-reinforced resin layers are formed from the same materials as the structural pipe wall and is applied in the same manner as that selected to form the structural pipe wall. Like the release layers, the number of fiber-reinforced resin layers that are applied depends on the particular fire pipe application and the degree of heat or flame resistance desired.

The jacket surrounding the structural pipe wall may comprise repeating release layers that are each formed from the same or different materials. For example, a fire resistant pipe may have a jacket comprising release layers the are formed from progressively more energy absorbing materials moving from the structural pipe wall to the outermost fiber-reinforced resin layer, to thereby provide a graduated degree of heat protection with the highest protection located where it is needed most, i.e., nearest the outermost surface of the pipe. In such an embodiment, it is desired that the material selected to form an outermost release layer have a relatively higher vaporization temperature than the remaining release layers that would be below the degradation temperature of the adjacent fiber-reinforced resin layers.

Additionally, the jacket surrounding the structural pipe wall may comprise an outermost fiber-reinforced resin layer having, as a filament component, at least one carbon fiber winding for purposes of holding the jacket together during pipe exposure to fire temperatures that exceed the melting temperature of glass filament.

Although the construction of fire resistant pipe embodiments have been specifically described and illustrated above, it is to be understood that this invention also includes the construction of fire resistant pipe fittings. Referring to FIGS. 7A to 7C, fire resistant pipe fittings, such as elbows 48, tees 50, Y-shaped fittings 52, and the like are also prepared according to principles of this invention.

Fire resistant pipes and pipe fittings of this invention can be used alone or combined to form a pipe assembly well suited for use in fire fighting pipe applications, such as fire fighting pipe assemblies that are used on offshore platforms and the like. Pipes and pipe fittings used in such applications must be able to function under conditions of high

1 temperature and close flame vicinity without suffering significant reductions in hoop strength and longitudinal strength.

5 Fire resistant pipes and pipe fittings constructed according to principles of this invention were subjected to a rigorous high-temperature to qualify for use in fire fighting piping applications. The test involved placing the pipe and/or pipe fittings approximately four inches from a 1,000°C flame with the pipe dry, i.e., with no water contained therein, for a period of approximately five minutes. After five minutes, the pipe and/or pipe fittings were filled with water at a rated pressure of approximately 300 psig (21 Kgf/cm²) for approximately fifteen minutes while still subjected to the flame.

10 To qualify for use in a fire fighting pipe application, the pipe and/or pipe fittings must remain structurally sound when subjected to rated pressure and not show signs of leakage in excess of ten percent of the rated pipe flow. In order to determine the total pressure withstanding ability of pipes subjected to such extreme temperature conditions, and to better understand the mechanism for heat related failure, the pressure was increased on pipe and pipe fitting samples that showed no signs of pipe leakage or structural damage beyond the rated pressure until pipe failure.

15 The following examples illustrate different fire resistant pipe embodiments constructed according to principles of this invention, and/or the test results for each pipe embodiment. In each of the following examples the pipe has an inside diameter of approximately two inches.

Example No. 1 - Fiber-Reinforced Pipe

25 A fiber-reinforced pipe was constructed using twelve layers of a fiber-reinforced resin, forming a wall thickness of approximately 0.37 centimeters (cm). The structural pipe wall was formed using fiberglass reinforcing fiber windings bonded together with a siloxane-modified phenolic resin, comprising approximately 83 percent by weight BP-J2027L (phenolic resole resin), 9 percent by weight SY-231 (methoxy-functional silicone intermediate), 7 percent by weight Phencat 381 (latent acid catalyst), 0.6 percent by weight Melacure Cotlin T-1 (organotin catalyst), and 0.4 percent by weight ethyl aminoethanol (amine catalyst). This pipe did not include a fire resistant layer.

30 The pipe was subjected to the above-identified test and showed signs of water leakage at a rate of approximately 0.008 cubic meters per hour (m³/h) at line pressure, and leaked water at a rate of approximately 0.21 m³/h when pressurized to between 14 to 21 Kgf/cm². The pipe failed at a pressure of approximately 35 Kgf/cm². The mode of pipe failure was a rupture in the fiber-reinforcing component of the structural pipe wall.

1 **Example No. 2 - First Embodiment Fire-Resistant Pipe**

 A fiber-reinforced pipe was constructed in a similar manner as that described for Example No. 1, except that the structural pipe wall thickness was approximately 0.40 cm. Additionally, the pipe was constructed having two fire resistant layers disposed around the
5 outside surface of the structural pipe wall. The fire resistant layers were formed from C-Veil impregnated with the same resin blend that was used to form the structural pipe wall. The fire resistant layers had a total wall thickness of approximately 0.21 cm.

 The pipe was subjected to the above-identified test and showed slight signs of water leakage at a rate of approximately $0.0045 \text{ m}^3/\text{h}$ at line pressure, and leaked water at a rate
10 of approximately $0.025 \text{ m}^3/\text{h}$ when pressurized to between 14 to 21 Kgf/cm^2 . The pipe failed at a pressure of approximately 84 Kgf/cm^2 . The mode of pipe failure was a rupture in the fiber-reinforcing component of the structural pipe wall. This pipe construction did not pass the test but displayed an improved resistance to the effects of the flame test when compared to the fiber reinforced pipe of Example No. 1.

15

Example No. 3 - First Embodiment Fire Resistent Pipe

 A fiber-reinforced pipe was constructed in a similar manner as that described for Example No. 1, except that the structural pipe wall thickness was approximately 0.38 cm. Additionally, the pipe was constructed having four fire resistant layers disposed around the
20 outside surface of the structural pipe wall. The fire resistant layers were formed from the same materials as that described for Example No. 2. The fire resistant layers had a total wall thickness of approximately 0.33 cm.

 The pipe was subjected to the above-identified test and showed no signs of water leakage at line pressure, showed slight signs of water leakage at a rate of approximately
25 $0.016 \text{ m}^3/\text{h}$ when pressurized to approximately 31.6 Kgf/cm^2 . The pipe failed at a pressure of approximately 126 Kgf/cm^2 . The mode of pipe failure was cracking in the resin matrix of the structural pipe wall and resulting leakage. No structural failure of the fiber reinforcement occurred. This example illustrates the improved heat resistance provided by two additional fire resistant layers when compared to Example No. 2.

30

Example No. 4 - First Embodiment Fire Resistent Pipe

 A fiber-reinforced pipe was constructed in a similar manner as that described for Example No. 1, except that the structural pipe wall thickness was approximately 0.36 cm. Additionally, the pipe was constructed having eight fire resistant layers disposed around the
35 outside surface of the structural pipe wall. The fire resistant layers were formed from a Nexus material impregnated with the same resin as that described for Examples Nos. 2 and 3. The fire resistant layers had a total wall thickness of approximately 0.2 cm.

1 The pipe was subjected to the above-identified test and showed slight signs of water
leakage at a rate of approximately 0.02 psig, showed signs of water leakage at a rate of
approximately 0.04 m³/h when pressurized to between 14 to 21 Kgf/cm². The pipe failed
5 at a pressure of approximately 80 Kgf/cm². The mode of pipe failure was a rupture in the
fiber component of the structural pipe wall. This example illustrates the relatively improved
heat resistance afforded by the C-Veil fire resistant layers of Example No. 2, and
demonstrates the improved heat resistance provided by the Nexus fire resistant layers when
compared with the non-protected pipe of Example No. 1.

10 Example No. 5 - First Embodiment Fire Resistant Pipe

A fiber-reinforced pipe was constructed having six layers of fiber-reinforced resin of
the same fiber and resin components disclosed above for Example No. 1, and having a wall
thickness of approximately 0.18 cm. Additionally, the pipe was constructed having four fire
resistant layers disposed around the outside surface of the structural pipe wall. The fire
15 resistant layers were formed from the same materials as that described for Example Nos. 2
and 3. The fire resistant layers had a total wall thickness of approximately 0.33 cm.

The pipe was subjected to the above-identified test and leaked water at a rate of
approximately 0.032 m³/h at line pressure, and leaked water at a rate of approximately 0.31
m³/h when pressurized to between 14 to 21 Kgf/cm². The pipe failed at a pressure of
20 approximately 35 Kgf/cm². The mode of pipe failure was a rupture in the fiber component
of the structural pipe wall. When compared to Example No. 3, this example illustrates the
improved heat resistance that is achieved when the structural pipe wall is formed from twelve
rather than six fiber-reinforced resin layers.

25 Example No. 6 - First Embodiment Fire Resistant Pipe

A fiber-reinforced pipe was constructed having twelve layers of a fiber-reinforced resin
of the same fiber and resin components disclosed above for Example No. 1. The structural
pipe wall had a wall thickness of approximately 0.38 cm. The pipe was constructed having
two fire resistant layers disposed around the outside surface of the structural pipe wall. The
30 fire resistant layers were formed from C-Veil impregnated with the same resin that was used
to form the structural pipe wall. The fire resistant layers had a total wall thickness of
approximately 0.18 cm.

The pipe was subjected to the above-identified test and showed no signs of water
leakage at line pressure, and showed slight signs of water leakage at a rate of approximately
35 0.007 m³/h when pressurized to between 14 to 21 Kgf/cm². The pipe failed at a pressure
of approximately 112 Kgf/cm². The mode of pipe failure was cracking in the resin matrix
of the structural pipe wall. No structural failure of the fiber reinforcement occurred. This

- 1 pipe construction displayed an improved resistance to the effects of the flame test when compared to the pipe of Example No. 2.

Example No. 7 - First Embodiment Fire Resistant Pipe

- 5 A fiber-reinforced pipe was constructed in the same manner as that described for Example No. 6, having twelve layers forming the structural pipe wall. The pipe was constructed having four fire resistant layers disposed around the outside surface of the structural pipe wall. The fire resistant layers were formed from the same materials described for Example No. 6, having a total wall thickness of approximately 0.33 cm.

- 10 The pipe was subjected to the above-identified test and showed no signs of water leakage at line pressure, and showed slight signs of water leakage at a rate of approximately $0.009 \text{ m}^3/\text{h}$ at a pressure of approximately $63 \text{ Kg}/\text{cm}^2$. The pipe failed at a pressure of approximately $133 \text{ Kg}/\text{cm}^2$. The mode of pipe failure was a rupture in the fiber component of the structural pipe wall. This pipe construction displayed an improved resistance to the effects of the flame test when compared to the pipe of Example No. 3.

Example No. 8 - First Embodiment Fire Resistant Pipe

- 20 A fiber-reinforced pipe was constructed in the same manner as that described for Example Nos. 6 and 7, having twelve layers forming the structural pipe wall, and having a wall thickness of approximately 0.38 cm. The pipe was constructed having six fire resistant layers disposed around the outside surface of the structural pipe wall. The fire resistant layers were formed from the same materials described for Example Nos. 6 and 7, having a total wall thickness of approximately 0.45 cm.

- 25 The pipe was subjected to the above-identified test and showed no signs of water leakage at line pressure, and showed slight signs of water leakage at a rate of approximately $0.004 \text{ m}^3/\text{h}$ at a pressure of approximately $60 \text{ Kg}/\text{cm}^2$. The pipe failed at a pressure of approximately $161 \text{ Kg}/\text{cm}^2$. The mode of pipe failure was discovered to cracking of the resin matrix of the structural pipe wall. No structural failure of the fiber reinforcement occurred. This example illustrates the improved heat resistance afforded by six fire resistant layers when compared to the fire resistant pipe of Example No. 7, having four fire resistant layers.

Example No. 9 - First Embodiment Fire Resistant Pipe

- 35 A fiber-reinforced pipe was constructed in the same manner as that described for Example Nos. 6, 7 and 8, having twelve layers forming the structural pipe wall, and having a wall thickness of approximately 0.37 cm. The pipe was constructed having eight fire resistant layers disposed around the outside surface of the structural pipe wall. The fire

1 resistant layers were formed from the same materials described for Example Nos. 6, 7 and
8, having a total wall thickness of approximately 0.55 cm.

5 The pipe was subjected to the above-identified test and showed no signs of water
leakage at line pressure, and showed no signs of water leakage at a pressure of
approximately 204 Kgf/cm². The pipe failed at a pressure of approximately 250 Kgf/cm².
The mode of pipe failure was cracking of the resin matrix of the structural pipe wall. Again,
no structural failure of the fiber reinforcement occurred. This example illustrates the
improved heat resistance afforded by eight fire resistant layers when compared to the fire
resistant pipe of Example No. 8, having six fire resistant layers.

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Example No. 10 - First Embodiment Fire Resistant Pipe

15 A fiber-reinforced pipe was constructed in the same manner as that described for
Example Nos. 6-9, having twelve layers forming the structural pipe wall, and having a wall
thickness of approximately 0.37 cm. The pipe was constructed having a total of six fire
resistant layers disposed around the outside surface of the structural pipe wall. The fire
resistant layers comprise, moving outwardly away from the structural pipe wall, two layers
of C-Veil, followed by two layers of Nexus, followed by two layers of C-Veil. The resin
component for each of the fire resistant layers is the same as that used to form the structural
pipe wall. The fire resistant layers have a total wall thickness of approximately 0.35 cm.

20 The pipe was subjected to the above-identified test and showed no signs of water
leakage at line pressure, and showed slight signs of water leakage at a rate of approximately
0.025 m³/h at a pressure of approximately 77 Kgf/cm². The pipe failed at a pressure of
approximately 147 Kgf/cm². The mode of pipe failure was cracking of the resin matrix of
the structural pipe wall. This example illustrates the improved heat resistance afforded by
25 using a combination of different fire resistant layers when compared to the fire resistant pipe
of Example No. 8, having six of the same type of fire resistant layers.

Example No. 11 - First Embodiment Fire Resistant Pipe

30 A fiber-reinforced pipe was constructed in the same manner as that described for
Example Nos. 6-10, having twelve layers forming the structural pipe wall, and having a wall
thickness of approximately 0.41 cm. The pipe was constructed having a total of eight fire
resistant layers disposed around the outside surface of the structural pipe wall. The fire
resistant layers were all formed from the Nexus material immersed in the same resin
component as that used to form the structural pipe, and had a total wall thickness of
35 approximately 0.22 cm.

The pipe was subjected to the above-identified test and showed slight signs of water
leakage at line pressure, and showed slight signs of water leakage at a rate of approximately
0.016 m³/h at a pressure of between 14 to 21 Kgf/cm². The pipe failed at a pressure of

- 1 approximately 91 Kgf/cm². The mode of pipe failure was a rupture in the fiber component of the structural pipe wall.

Example No. 12 - Second Embodiment Fire Resistant Pipe

- 5 A fiber-reinforced structural pipe was constructed using the same fiber and resin components as that used in the previous examples. The structural pipe wall was formed from twelve layers of the fiber-reinforced resin and had a wall thickness of approximately 0.4 cm. The pipe was constructed having a total of eight layers of polyethylene disposed around the outside surface of the structural pipe wall. The polyethylene layers had a total wall thickness of approximately 1.2 millimeters. A total of four outside fiber-reinforced resin layers were formed from the same materials as the structural pipe wall, and were disposed around the outside surface of the polyethylene layer. The outside fiber-reinforced resin layers had a total wall thickness of approximately 0.13 cm.

- 15 The pipe was subjected to the above-identified test and showed no signs of water leakage at line pressure, and no signs of leakage at twice the rated pressure (21 Kgf/cm²). The pipe showed first signs of leakage at approximately 108 Kgf/cm², leaking at a rate of approximately 31 m³/hr. The pipe failed at a pressure of approximately 715 Kgf/cm². The mode of pipe failure was a rupture in the fiber component of the structural pipe wall. This example illustrates the improved heat resistance afforded by using the polyethylene energy absorbing material layer in place of the fire resistant layer.

Example No. 13 - Fiber-Reinforced Pipe

- 25 A two inch (51 millimeter) diameter fiber-reinforced structural pipe wall was constructed comprising approximately twelve layers of a fiber-reinforced resin, prepared as set forth in Example No. 1 above. The impact resistance of the structural pipe wall was tested by dropping a 60 mm steel ball, weighing 0.9 kg from progressive heights to impact the pipe perpendicularly. After the impacts were completed the pipe was pressurized with air at a pressure of 25 psig and held under water for detection of visible air leaks.

- 30 Under these test conditions theunjacketed structural pipe wall displayed a 75 percent probability of failure, i.e., three of the four impacts leaked air, after four drops from a ball drop height of approximately 10 inches (25 centimeters). The same unjacketed structural pipe wall displayed complete or a 100 percent probability of failure, i.e., each of the four impacts leaked air, after four drops when the ball drop height was further increased to 12 inches (30 centimeters).

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Example No. 14 - Third Embodiment Fire Resistant Pipe

A two inch diameter structural pipe wall was constructed according to Example No. 13 above, and a jacket was disposed around the structural pipe wall to form a fire resistant

1 pipe. The jacket was formed from approximately four each repeating layers of polypropylene
tape and fiber-reinforced resin. The fiber-reinforced resin layers were formed from the same
materials used to form the structural pipe wall.

5 The impact resistance of the fire resistant pipe so formed was tested according to the
above-described method. The fire resistant pipe did not display any signs of air leakage, i.e.,
zero percent probability of failure, until a ball drop height of approximately 35 inches (100
centimeters) was reached. At 35 inches, only one impact out of eight showed any signs of
leakage. At drop heights of 40 and 54 inches, only three impacts out of eight and Therefore,
a fifty percent probability of failure for the jacketed pipe was observed to occur at
10 approximately 45 inches, compared to 10 or 11 inches with the unjacketed structural pipe
wall. Accordingly, based on such test data, the jacketed pipe displayed a 400 percent
improvement in impact resistance when compared to a unjacketed pipe.

Although specific embodiments and examples of fire resistant pipes and pipe fittings
have been described and illustrated, many modifications and variations will be apparent to
15 those skilled in the art. It is, therefore, to be understood that, within the scope of the
appended claims, fire resistant pipe and pipe fittings of this invention can be constructed
other than as specifically described herein.

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1 **What is Claimed is:**

1. A fire resistant pipe comprising:

5 a structural wall comprising layers of helically wound reinforcing fiber bonded with a resin selected from the group consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures thereof; and

10 at least one fire resistant layer overlying the structural wall, wherein the fire resistant layer includes a fibrous carrier component impregnated with a resin selected from the group consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures thereof, and wherein the resin selected to form the fire resistant layer is compatible with the resin selected to form the structural wall.

2. A fire resistant pipe as recited in claim 1 wherein the resins selected to form the structural wall and the fire resistant layer are the same.

15 3. A fire resistant pipe as recited in claim 1 wherein the fire resistant layer comprises at least 75 percent by weight resin.

20 4. A fire resistant pipe as recited in claim 1 wherein the resin used to form the structural wall and the fire resistant layer are both siloxane-modified phenolic resins, and wherein the fire resistant layer comprises at least three times the resin content as the helically wound reinforcing fiber forming the structural wall.

25 5. A fire resistant pipe as recited in claim 1 comprising a number of energy absorbing material layers interposed between the structural wall and the fire resistant layer.

6. A fire resistant pipe comprising:

30 a structural wall comprising layers of helically wound reinforcing fiber bonded with a resin selected from the group consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures thereof;

35 a number of energy absorbing material layers overlaying the structural wall, wherein the energy absorbing material is selected from the group consisting of materials capable of absorbing energy by phase transformation at a temperature below a degradation temperature of the structural wall; and

 a number of fiber-reinforced resin layers disposed over an outside surface of the energy absorbing material layers, wherein resin component is selected from the same group of resins used to form the structural wall.



- 1 7. A fire resistant pipe as recited in claim 6 wherein the resin is a siloxane-
modified phenolic resin prepared by combining:
 a major proportion of phenolic resole or phenolic novolac resin;
 a minor proportion of silicone intermediate; and
5 a sufficient amount of catalyst to facilitate processing and effect cure.
8. A fire resistant pipe comprising:
 a structural wall comprising layers of helically wound reinforcing fiber bonded with
a resin selected from the group consisting of phenolic resins, siloxane-modified phenolic
10 resins, furan resins, and mixtures thereof; and
 a jacket disposed around the structural wall, the jacket comprising:
 at least one release layer of material that is chemically incompatible with the
resin used to form the structural wall; and
 at least one fiber-reinforced resin layer disposed around a surface of the release
15 layer.
9. The fire resistant pipe as recited in claim 8 wherein the jacket comprises a
number of alternating release and fiber-reinforced resin layers.
- 20 10. The fire resistant pipe as recited in claim 8 wherein the fiber-reinforced resin
layer comprises helically wound reinforcing fibers bonded with a resin selected from the
group consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and
mixtures thereof.
- 25 11. The fire resistant pipe as recited in claim 8 wherein the release layer is formed
from a polyolefinic material.
12. A fire resistant pipe as recited in claim 8 wherein the resin used to form the
structural wall and the fire resistant layer are both siloxane-modified phenolic resins.
30
13. A fire resistant pipe comprising:
 a structural wall comprising layers of helically wound reinforcing fiber bonded with
a resin selected from the group consisting of phenolic resins, siloxane-modified phenolic
resins, furan resins, and mixtures thereof;
35 a jacket disposed around the structural wall, wherein the jacket comprises a number
of alternating release layers and fiber-reinforced resin layers, wherein a fiber-reinforced resin
layer forms an outermost pipe layer, and wherein the release layers are formed from a



1 material that is incapable of forming a bond with the resin component of the structural wall
and the fiber-reinforced layers.

5 14. The fire resistant pipe as recited in claim 13 wherein the fiber-reinforced resin
layer comprises layers of helically wound reinforcing fiber bonded with a resin selected from
the group consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and
mixtures thereof.

10 15. A fire resistant pipe comprising:
a structural wall comprising layers of helically wound reinforcing fiber bonded with
a resin selected from the group consisting of phenolic resins, siloxane-modified phenolic
resins, furan resins, and mixtures thereof; and
a jacket disposed around the structural wall, the jacket comprising:
15 at least one release layer of material that is chemically incompatible with the
resin used to form the structural wall; and
at least one fiber-reinforced resin layer disposed around a surface of the release
layer, wherein the fiber-reinforced resin layer comprises helically wound reinforcing
fiber bonded with a resin selected from the group consisting of phenolic resins,
siloxane-modified phenolic resins, furan resins, and mixtures thereof, and wherein the
20 release layer is formed from a material that is chemically incompatible with the resin
used to form the fiber-reinforced resin layer.

25 16. A fire resistant pipe comprising:
a structural wall comprising layers of helically wound reinforcing fiber bonded with
a resin selected from the group consisting of phenolic resins, siloxane-modified phenolic
resins, furan resins, and mixtures thereof;
a jacket disposed around the structural wall, wherein the jacket comprises a number
of alternating release layers and fiber-reinforced resin layers, wherein a release layer is
disposed around an outside surface of the structural wall, wherein a fiber-reinforced resin
30 layer forms an outermost pipe layer, wherein each fiber-reinforced resin layer comprises a
reinforcing fiber bonded with the same resin used to form the structural wall, and wherein
each release layer is formed from a material that is incapable of forming a bond with the
resin component of the structural wall and the fiber-reinforced layers.

35 17. The pipe as recited in claim 16 wherein the material used to form the release
layer is selected from the group consisting of materials capable of absorbing energy by phase
transformation at a temperature below a degradation temperature of the structural wall.



- 1 18. A method for forming a fire resistant pipe comprising the steps of:
 helically winding reinforcing fiber wetted with a resin selected from the group
 consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures
 thereof, for forming a structural pipe wall;
5 placing a fibrous carrier wetted with the same resin over the structural pipe wall, for
 forming a fire resistant layer; and
 curing the resin in both the structural pipe wall and the fire resistant layer to form a
 bond therebetween.
- 10 19. A method for forming a fire resistant pipe comprising the steps of:
 helically winding a reinforcing fiber wetted with a first resin for forming a structural
 pipe wall, wherein the first resin is selected from the group consisting of phenolic resins,
 siloxane-modified phenolic resins, furan resins, and mixtures thereof; and
 winding a fibrous carrier wetted with a second resin around the structural pipe wall
15 for forming a fire resistant layer, wherein the second resin is selected from the group
 consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures
 thereof, wherein the second resin is compatible with the first resin, and wherein the carrier
 comprises at least 75 percent by weight of the second resin.
- 20 20. A method for forming a fire resistant pipe comprising the steps of:
 helically winding reinforcing fiber wetted with a resin selected from the group
 consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures
 thereof, for forming a structural pipe wall;
 placing a number of energy absorbing layers over the structural pipe wall, wherein the
25 energy absorbing layers are formed from materials selected from the group consisting of
 materials capable of absorbing energy by phase transformation at a temperature below a
 degradation temperature of the structural pipe wall; and
 helically winding a number of fiber-reinforced resin layers over the energy absorbing
 layers, wherein the resin component used to form the fiber-reinforcing layers is selected from
30 the same group of resins used to form the
 structural pipe wall.
21. A method for forming a fire resistant pipe comprising the steps of:
 helically winding reinforcing fiber wetted with a resin selected from the group
35 consisting of phenolic resins, siloxane-modified phenolic resins, furan resins, and mixtures
 thereof, for forming a structural pipe wall;
 forming a jacket around an outside surface of the structural pipe wall by placing a
 release material around the outside surface of the structural pipe wall, and placing a fiber-



- 1 reinforced resin layer over the release material, wherein the release material is formed from
a material that is incapable of forming a bond with resins used to form both the structural
pipe wall and the fiber-reinforcer resins layer; and
5 curing the resin in both the structural pipe wall and the fiber-reinforced resin layer.

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