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(54) Title: AN ANTISLOSH, ANTISTATIC, AND FLAME ARRESTING STRUCTURE FOR USE WITH CONTAINERS FOR HOLDING FLAMMABLE FLUIDS (57) Abstract An antistatic, fibrous structure for use in or with containers holding flammable liquids comprising a multiplicity of substantially irreversibly heat set carbonaceous fibres having a carbon content of greater than 65 percent by weight and an LOI value greater than 40, said carbonaceous fibers being present in an amount effective for preventing sloshing of the fluids and capable of arresting a flame front.		

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AN ANTISLOSH, ANTISTATIC, AND FLAME ARRESTING STRUCTURE
FOR USE WITH CONTAINERS FOR HOLDING FLAMMABLE FLUIDS

The present invention relates to an antislosh, antistatic, flame arresting structure for use with containers holding flammable fluids and to a process
5 for arresting flames in or about the container.

More particularly, the invention is concerned with resilient, shape reforming, lightweight, nonflammable structures of carbonaceous fibers having
10 the ability to control or stop sloshing of fuel in a fuel container, act as a flame arrester, and prevent and/or dissipate the buildup of static electricity. The structures are further characterized by having good chemical and hydrolytic inertness and are stable to
15 long periods of exposure to the flammable fluids.

For many years the handling and use of flammable fluids such as liquid fuels, combustible gases and other combustible chemicals or intermediates
20 have posed serious potential hazards of fire and explosion due to an electrostatic buildup during filling or unloading of containers, such as tanks, due to triboelectric generated discharge or due to sloshing
25 of the liquids back and forth in the tanks during

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transportation of the tanks. Transporting tanks which partially contain flammable liquids, or which contain a small amount of liquid to the extent that the tank is essentially empty, poses the additional hazard of explosion of the liquid and/or gaseous by-products due to sparking or static electric discharge caused by the sloshing (rapid movement) of the liquid inside the tank. Methods used to prevent sparking and/or static discharge in the tank include padding the tank with an inert gas or adding a flame arresting system to the tank. In addition, physical grounding has been the customary technique for reducing this hazard. However, this technique has not eliminated the problem completely. In addition, human error and poor electrical connections have led to explosions resulting in loss of human life and equipment.

In more recent times, containers have been filled with a reticulated open cell polymeric foam in an effort to eliminate the above problems and hazards. One class of foam used heretofore is a polyether urethane which has good chemical resistance, but which has poor electrostatic dissipating properties and which is flammable in the presence of air. Electrostatic ignition could take place due to triboelectric generation if a container with the polyether urethane foam was to rupture due to stress or on impact with another object. The other class of foam used heretofore is a polyester urethane which has fairly good electrostatic dissipating properties, but has poor hydrolytic properties, poor solvent stability and is also fairly flammable in air. Both of the above classes of foams lose their structural properties when

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exposed to hydrocarbon fuels over a period of time and thus must be replaced regularly.

5 However, mere sloshing of a liquid is not the only source of electrostatic buildup, and therefore the control of sloshing and, in turn, the control of the electrostatic buildup created by the sloshing alone does not solve the other problems encountered in fuel tank usage. For example, since foam materials are not
10 good electrical conductors, they do not discharge an electrostatic buildup such as that generated during filling and emptying of a container. In addition, such foams are weak structurally and exhibit slow
15 degradation in the presence of most flammable liquids, especially hydrocarbon liquids. This instability problem is increased when a small amount of moisture is present in the container and contacts the foam. Another problem frequently encountered in the use of
20 containers with flammable liquids and/or gases is cracking or rupturing of the containers due to impact or material fatigue. A crack or rupture in a container will allow the flammable fluids to freely escape and pose a dangerous and hazardous condition.

25 While some success has been obtained by the use of the above-mentioned foams, it would be advantageous for the industry to have a material which, in addition to preventing sloshing, is stable in the presence of
30 flammable fluids, exhibits high electrical conductivity sufficient to dissipate electrostatic buildup and acts as a flame arrester in instances where a spark could occur. Further, it is desirable to have a material
35 which is substantially flame resistant and has the capability, when used as an outer liner for a container, of greatly retarding the escape of a

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flammable liquid from the container should the container leak or rupture. Such a novel material is described hereinafter in the accompanying specification and examples. All percentages set forth hereinafter
5 are in percent by weight unless otherwise specified.

In accordance with the present invention there is provided a lightweight, nonflammable structure comprising a multiplicity of irreversibly heat set,
10 continuous or staple, carbonaceous fibers, in the form of a wool-like fluff, batting, webbing or the like.

The fibers are formed by a partial carbonization of stabilized polymeric fibers or fabric
15 or some other stabilized carbon fiber precursor material, such as acrylic fibers or pitch fibers, under conditions to impart a substantially irreversible, nonlinear, e.g., sinusoidal or coil-like,
20 configuration, to the fibers as will be hereinafter described. The fibers are further characterized by their wool-like fluffy appearance and texture when formed into a nonwoven structure such as, for example, a mat or batting. As will become apparent, the greater
25 the amount of coil-like fibers present in the structure, the greater will be the wool-like texture and resilience. The fibers may be blended with noncarbonaceous fibers or linear carbonaceous fibers.

30 The carbonaceous fibers are preferably nonlinear but may also include blends of nonlinear and linear carbonaceous fibers. The carbonaceous fiber structures of the invention possess excellent
antistatic, antislashing and flame arresting
35 properties. Advantageously, the structure comprises a multiplicity of resilient carbonaceous fibers having a

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sinusoidal or coil-like shape with a reversible deflection ratio of at least about 1.2:1, an aspect ratio (1/d) of greater than 10:1 and a LOI (limited oxygen index) of greater than 40. The carbonaceous
5 fiber structure when in the form of a wool like fluff is extremely lightweight and has a bulk density of from 2.4 to 32 kg/m³, preferably from 2.4 to 8.0 kg/m³.

More particularly, the invention resides in a
10 flame arresting structure for use with containers for holding flammable fluids comprising a multiplicity of nonflammable, substantially irreversibly heat set, carbonaceous fibers having an LOI value greater than
15 40, said carbonaceous fibers being present in an amount effective for arresting a flame front.

The carbonaceous fiber structure is present on the inside of the container in an amount effective to prevent sloshing of the flammable fluid and also to
20 prevent the buildup of an electrostatic charge in the container which could generate a spark to ignite the fuel. The fuel in the container may be entirely liquid or entirely gaseous. When the fuel is in a liquid
25 form, there is usually a zone above the liquid level in the container which is in a gaseous state and, therefore, is also highly flammable. Optionally, the carbonaceous fiber structure is also present on the outside of the container, i.e. on at least one outer
30 surface of the container, in an amount effective to arrest a flame front extending from a rupture in the container. The term "amount effective" used herein is used in a broad sense since the amount depends on the density of the fibrous structure and its location on
35 the inside or on the outside of the container. The density of the fibrous structure, in turn, will vary

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depending upon the amount of fluid flow desired. The fluid flow from a fuel tank to power an aircraft engine, for example, may be relatively high, requiring a relatively high flow of fuel from the tank.

5

The invention also resides in a container for holding a flammable liquid and/or gas, wherein the inside of said container contains a carbonaceous fiber structure in an amount sufficient to substantially
10 retard sloshing of the liquid within the container but without preventing the flow of liquid from the container, and wherein at least a portion of an outer surface of said container is covered with a flame
15 arresting carbonaceous fiber structure in an amount sufficient to arrest a flame front of the flammable liquid and/or gas passing through a rupture in the container.

20

The present invention is specifically concerned with structures comprising a multiplicity of the nonflammable carbonaceous fibers which are particularly identified by their degree of carbonization and/or their degree of electrical conductivity in the
25 determination of the particular use for which they are most suited.

30

Carbonaceous fibers that are derived from nitrogen containing polymeric materials, such as an acrylic based polymer, generally have a nitrogen
30 content of from 5 to 35 percent, preferably from 16 to 25 percent, more preferably from 18 to 20 percent.

35

The "electrical resistance" of a carbonaceous fiber is determined by measurement on a 6K tow of
35 fibers with the individual fibers having a nominal

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diameter of from 7 to 20 microns. The "specific resistivity is calculated by measurements as described in European Patent Application Serial No. 0199567.

5 The carbonaceous fibrous material which is utilized in the composite structures of this invention may be classified into three groups depending upon the particular use and the environment that the structures in which they are incorporated are placed.

10 In accordance with one embodiment of the invention, the carbonaceous fibers which are utilized in antistatic, flame arresting and antislosh applications are electrically nonconductive and possess
15 no antistatic characteristics, i.e., they are not able to dissipate an electrostatic charge. The nonconductive fibers have an electrical resistance of greater than 4×10^6 ohms/cm and, correspondingly, a specific resistivity of greater than 10^{-1} ohm-cm. When
20 the nonconductive fibers are selected from an acrylic polymer, it was determined that the nitrogen content of such fibers was greater than about 18 percent.

25 In accordance with a second embodiment of the invention, the carbonaceous fibers which are utilized in the structures of the invention are partially electrically conductive, i.e., have a low degree of electrical conductivity, and a carbon content of less
30 than 85 percent. The electrical resistance of these fibers is generally from 4×10^6 to 4×10^3 ohms/cm. Preferably, the carbonaceous fibers are derived from stabilized acrylic fibers and possess a nitrogen content of from 16 to 20 percent. The larger the
35 amount of carbon content of the fibers utilized, the higher the degree of electrical conductivity. These

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higher carbon content filaments still retain a wool-like appearance when formed into a mat or a batting especially when the majority of the fibers are nonlinear in shape. Also, as will become apparent, the greater the percentage of nonlinear fibers in the structure, the greater is the resiliency or loft of the structure. As a result of the greater carbon content, the structures prepared with these fibers have greater static dissipating and antislash properties and result in effective flame arresters even at higher temperatures of use.

In accordance with a third embodiment of the invention, the carbonaceous fibers which are utilized in the antislash and/or flame arresting structures of the invention have a carbon content of at least 85 percent. Preferably, the filaments which are utilized are derived from stabilized acrylic fibers and have a nitrogen content of less than 16 percent. As a result of the still higher carbon content, structures prepared from such fibers have a higher electrical conductivity. That is, the resistance is less than 4×10^3 ohms/cm. Correspondingly, the specific resistivity is less than 10^{-1} ohms/cm.

The highly conductive fibers can be utilized in place of conventional straight or linear carbon fibers. Moreover, the coil-like carbonaceous fibers, when formed into a structure such as a mat or batting, provide a better ability to electrically ground and thus prevent the buildup of static electricity and the generation of sparks. A structure containing a greater amount of coil-like fibers, as opposed to sinusoidal or

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linear fibers, provides a more effective barrier against the spread of flame fronts.

5 Linear heat set carbonaceous fibers which are utilized in antistatic, antislosh and/or flame arresting applications are comprised of fibers formed from the same stabilized precursor material as the nonlinear fibers with the exception that the step of irreversibly heat setting (thermosetting) the fibers is
10 done with the fiber precursor material held in a linear configuration. The linear carbonaceous fibers may be blended with and at least partially bonded to nonlinear thermoplastic or thermoset fibers or fiber blends in the form of a fluff, batting, web, or the like.

15 In accordance with the present invention, an open web or batting is provided consisting of randomly entangled, nonlinear carbonaceous fibers, as herein defined. The web is of a sufficient structural
20 strength to maintain its open web shape in the presence of flammable liquids such as liquid hydrocarbons and thus prevent sloshing of the liquid as well as to be substantially noncompacting. Various degrees of structural rigidity and stiffness of the web can be
25 obtained by bonding or curing a thermoplastic or thermoset material in the web. In addition, the product is fire or flame resistant and effectively acts as a wick and a flame block to prevent a mass of the
30 flammable liquid entrapped in the web from rapidly spilling out, thus reducing the chance of explosion. The tightness of the web of the invention can be varied such as to provide an increased holdup or retardation of liquid flow, or of a looseness such as to permit a
35 higher rate of liquid flow, depending on the particular use for the web. The web may also be fixed in its

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desired form and/or shape by cementing the juxtapositioned fibers one to the other leaving the web still very open, but of a more stable, less compressible body under load.

5

If desired, the structure may comprise a blend of linear carbonaceous fibers with thermoplastic or thermoset polymeric fibers or a fiber blend such as a polyester, or a blend of a high melting polyester with a smaller content of a lower melting polyester binder fiber in order to provide densification and/or some rigidity and integrity to the structure. It is also desirable for this structure to have a sufficient amount of carbonaceous fibers present to provide flame retardant properties.

15

Figure 1 is a cross-sectional view of a container for flammable fluids illustrating one embodiment of the present invention.

20

The antislush, flame arresting and/or antistatic fibrous structures of the invention are formed from nonflammable carbonaceous fibers, preferably fibers which are nonlinear and resilient, and which possess a reversible deflection ratio of greater than about 1.2:1 and an aspect ratio (1/d) of greater than 10:1. The nonlinear carbonaceous fibers may have a sinusoidal or a coil-like configuration or a more complicated structural combination of the two.

25

30

The fibers of the invention have a LOI value greater than 40, as determined by test method ASTM D 2863-77. The test method is also known as "oxygen index" or "limited oxygen index" (LOI).

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The carbonaceous fibers of the invention are prepared by heat treating a carbonaceous precursor material such as that derived from acrylic materials, pitch based materials, such as petroleum or coal tar, or other carbonaceous polymeric materials which can be made into linear or nonlinear carbonaceous fibers or fibrous structures which are thermally stable and highly flame resistant.

For example, in the case of polyacrylonitrile (PAN) based fibers, the fibers are formed by melt or wet spinning a suitable liquid of a precursor material having a normal nominal diameter of from 4 to 25 micrometers. The precursor material is collected as an assembly of a multiplicity of continuous filaments in tows and stabilized (by oxidation in the case of PAN based fibers) in the conventional manner. The oxidation stabilized tows (or staple yarn made from chopped or stretch broken fiber staple) may thereafter, in accordance with the present invention, be formed into a sinusoidal or other nonlinear shape by knitting or weaving the tow or yarn into a fabric or cloth (recognizing that other fabric forming and coil forming methods can be employed). The so-formed fabric or cloth is thereafter heat treated, with the fibers or fiber tow in a relaxed and unstressed condition, at a temperature of from 525°C to 750°C, in an inert atmosphere for a period of time sufficient to produce a heat induced thermoset reaction wherein additional cross-linking and/or a cross-chain cyclization reaction occurs between the original polymer chain. At the lower temperature range of from 150°C to 525°C, the fibers are provided with a varying degree of temporary to permanent set while in the upper range of

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temperatures of from 525°C and above the fibers are provided with a substantially permanent or irreversible heat set. It is understood that other methods of shape formation such as crimping and coiling combined with
5 thermosetting can be used.

What is meant by substantially permanently or irreversibly heat set is that the fibers possess a degree of irreversibility in their set nonlinear
10 configuration. More particularly, once a carbonaceous fiber is heat set in a nonlinear shape, it can be stretched to a substantially linear shape but will always return to its nonlinear shape once the tension on the fiber is released. It is, of course, to be
15 understood that the fiber or fiber assembly may be initially heat treated at the higher range of temperatures so long as the heat treatment is conducted while the coil-like and/or sinusoidal configuration is
20 in a relaxed or unstressed state and under an inert, nonoxidizing atmosphere. As a result of the higher temperature treatment, a heat set coil-like or sinusoidal configuration or structure is imparted to the fibers, yarns, tows or threads. The resulting
25 fibers, tows or yarns having the nonlinear structural configuration which are derived by deknitting the cloth, are subjected to other methods of treatment known in the art to create an opening. In such a procedure, the nonlinear fibers, yarn or tow of the
30 cloth are separated into an entangled, wool-like fluffy material in which the individual fibers retain their coil-like or sinusoidal configuration yielding a fluff or batting-like body of considerable loft.

35 The fluff or batting of the invention may be utilized alone or may be provided with a suitable

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barrier layer of flexible sheet material or metal depending upon its desired use.

5 The stabilized fibers when permanently shaped into the desired structural configuration, e.g., by knitting, and thereafter heating at a temperature of greater than about 550°C retain their resilient and reversible deflection characteristics. It is to be understood that higher temperatures may be employed of
10 up to about 1500°C, but the most flexible and the smallest loss of fiber breakage, when carded to produce the fluff, is found in those fibers and/or filaments that are heat treated to a temperature of from 525°C to
15 750°C.

 When the precursor stabilized fiber is an acrylic fiber, the percentage nitrogen content is generally from 16 to 25 percent. The fibers are excellent for use where electrical antistatic
20 properties are desired. The structures formed therefrom are lightweight, have low moisture absorbency, good abrasive strength together with good appearance and handle.

25 Carbonaceous fibers having a carbon content of at least 85 percent have superior thermal stability and flame arresting characteristics. The coil-like structure in the form of a fluff (when carded) provides
30 a web which has good compressibility and resiliency while maintaining improved flame arresting and electrical grounding capability. The structure prepared with such fibers have particular utility in high flammability applications where spark or
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electrostatic generation cannot be tolerated and in areas of high temperatures.

5 The precursor stabilized acrylic filaments which are advantageously utilized in preparing the fibers of the structures are selected from the group consisting of acrylonitrile homopolymers, acrylonitrile copolymers and acrylonitrile terpolymers. The copolymers preferably contain at least about 85 mole
10 percent of acrylonitrile units and up to 15 mole percent of one or more monovinyl units copolymerized with styrene, methylacrylate, methyl methacrylate, vinyl chloride, vinylidene chloride, vinyl pyridine and the like. Also, the acrylic filaments may comprise
15 terpolymers wherein the acrylonitrile units are at least about 85 mole percent.

 It is to be further understood that carbonaceous precursor starting materials may have
20 imparted to them an electrically conductive property on the order of that of metallic conductors by heating the fiber fluff or the batting-like shaped material to a temperature above 1000°C in a nonoxidizing atmosphere.
25 The electroconductive property may also be obtained from other selected starting materials such as pitch (petroleum or coal tar), polyacetylene, acrylonitrile based materials, e.g., a polyacrylonitrile copolymer (PANOX™ or GRAFIL-01™, trademarks of E. I. du Pont de
30 Nemours & Co., Inc.), polyphenylene, polyvinylidene chloride resin (SARAN™, a trademark of The Dow Chemical Company) and the like.

 A wool-like fluff of the carbonaceous fibers of
35 the invention may be treated with an organic or inorganic binder, needle punched, bagged or adhered to

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a flexible or rigid support using any of the conventional materials and techniques depending upon the use and environment of the structure. The fluff may be placed on the inside of a structure, such as a fuel tank, or between structural parts, such as a container liner and outside skin, either in the form of a mat, web, felt, batting, or similar structure. Advantageously, various degrees of structural rigidity and stiffness of the carbonaceous structure can be obtained by incorporating a bonded or cured thermoplastic or thermoset polymeric material in the structure. This is preferably accomplished by blending thermoset or thermoplastic polymeric fibers with the carbonaceous fibers of the invention prior to formation of the structure followed by curing or thermobonding, or by coating the web or fluff with a thermoplastic resinous material followed by curing. Also, other stiffening fibers such as, for example, high performance fibers may be blended with the carbonaceous fibers to enhance the stiffness and integrity of the web. Exemplary of high performance fibers are KEVLAR™ (an aromatic polyamide and a trademark of E. I. du Pont de Nemours & Co., Inc.), NOMEX™ (an aramid fiber and a trademark of E. I. du Pont de Nemours & Co., Inc.), meta aramid fibers, polybenzimidazole (PBI) fibers, and the like.

The coil-like or sinusoidal carbonaceous fibers and/or filaments are formed such that they are sufficiently electrically conductive to dissipate an electrostatic buildup before it achieves a dangerous level. In addition, the material is fire or flame resistant, effectively acts as a barrier to reduce the outflow of a flammable liquid from the container, and

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has the ability to act as a flame arrester should a leaking liquid from the container ignite, thus reducing the chance of explosion. The tightness of the web of the invention can be varied such as to provide a marked
5 holdup or retardation of liquid flow, or of a looseness to permit a high rate of liquid flow. The web may also be fixed in its desired form and/or shape by cementing the juxtapositioned fibers one to the other leaving the web still very open but of a more stable, less
10 compressible body under load.

In another preferred embodiment, it is desirable to have a layered construction, such as that illustrated in the figure. In this embodiment, layers
15 of the structure of the invention having varying degrees of stiffness, and hence varying degrees of fuel flow rates, are placed within the container, and a nonstiffened structure is placed between the inner
20 liner and outer wall of the container to retard the leakage of fuel and act as a flame arrester, should the container rupture.

If desired, the structure may also comprise a
25 thermoplastic polymeric fiber, such as polyester fiber, or the like, in order to provide densification, shape retention and extra rigidity of the structure.

Exemplary of the present invention are the
30 following examples.

Example 1

In this example, a fluff or wool-like structure
35 was prepared which is particularly useful in antislosh

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and flame arresting applications where electrical grounding of the structure is required.

5 Following the procedure disclosed in European Patent Application Serial No. 0199567, published October 29, 1986, to F. P. McCullough, et al entitled, "Carbonaceous Fibers with Spring-Like Reversible Deflection and Method of Manufacture," a 3K OPF (i.e., oxidized polyacrylic fiber having 3000 filaments)
10 PANOX™ stabilized tow was knit on a Singer flat bed knitting machine at a rate of 4 stitches/cm and was then heat treated at a temperature of 950°C. The cloth was deknitted and the tow (which had a coil elongation or reversible deflection ratio of greater than 2:1) was
15 cut into 7.5 cm length staple. The cut staple was then carded on a Platt Miniature carding machine to produce a wool-like fluff having fibers ranging from 2.5 cm to 6.5 cm in length. The wool-like fluff had a high
20 electrical conductivity (a resistance of less than 40 ohms/cm) over any length of up to 60 cm tested.

In lieu of PANOX™, there may be employed stabilized pitch based fibers or a copolymer or
25 terpolymer of polyacrylonitrile.

Example 2

In this example, a fluff or wool-like structure was prepared which is particularly useful in antislosh
30 and flame arresting applications where electrical grounding of the structure is required.

In a similar manner to Example 1, a portion from the same knit sock was heat treated at a
35 temperature of 1550°C. The cloth itself and the deknitted tow had a very high electrical conductivity.

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On carding 15 cm lengths of cut tow, a wool-like fluff was obtained which had fiber lengths of from 2.5 to 7.5 cm with average lengths of 5 cm. Thus, carding of a deknitted fabric of a continuous filament tow which has been subjected to a temperature of above 1000°C is still capable of producing a wool-like fluff product.

Example 3

10 In this example, a structure effective as an antislash, antistatic and flame arrester capable of arresting flame fronts from gasoline or naphtha vapors was produced as follows:

15 Using the procedure of Example 1, a 6K OPF tow was knitted into a fabric, the fabric treated at 650°C until it was thermally set and thereafter deknitted to produce a nonlinear carbonaceous fiber tow which was then cut into staple of from 14 to 17 cm nominal
20 lengths. This so-cut staple was opened on a Shirley opener and further processed on a Rando Webber machine, an air laying system for producing nonwoven batting. The feed plate and combing roll were spaced at a distance of 0.3 mm and dispersed into the chamber using
25 a 1200 rpm setting on the fan. Approximately 50 percent of 6 denier polyester fiber was blended with opened, nonlinear carbonaceous fibers in the preblending section of the Rando Webber. The resulting
30 batting was passed through a Benz hot air oven, held at a temperature of 260°C, at a rate of 2 m/minute resulting in an oven time of about 1 minute. This was sufficient to soften the polyester fibers to achieve a light bonding of the carbonaceous fibers in the web.
35 This structure had excellent antistatic and stiffness

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properties, and was found to be especially useful in applications where good fuel flow rates are required.

Example 4

5 A. In a manner similar to the procedure described in Example 3, the cut fibers were treated in a Shirley opener and then a Rando Webber air laying system, but with approximately 1 percent low melting
10 EAA (ethylene acrylic acid) binder fibers added.

 B. The fluff and/or batting of Part A was partially coated with an epoxy resin to form structures of varying rigidity. The fluff or batting was placed
15 on an expanded metal screen in a laboratory hood. A series of samples designated as Samples A to E were sprayed on all sides with a novolac epoxy resin (D.E.N.[™] 438, a trademark of The Dow Chemical Company) as a 20 percent solution in acetone to which had been
20 added (in a ratio of 28 to 100 of the amount of the epoxy used) methylene dianiline as a hardening agent. Sample F was sprayed on all sides with an aliphatic diepoxide resin (D.E.R.[™] 732) as a 20 percent solution
25 in methyl ethyl ketone to which had been added (in a ratio of 31:100 of the amount of the epoxide used) methylene dianiline as a hardening agent. After driving the acetone out of each sample under a heat lamp, the coated sample was placed in an oven at 105°C.
30 The temperature was increased to 125°C where it remained for approximately 1 hour. The oven temperature was then raised to 170°C and held thereat for an additional hour. Upon cooling, each sample was weighed to determine the percent resin content. Electrical

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resistance measurements were also made on each sample. The results are summarized in Table I as follows:

TABLE I

5	<u>Sample</u>	<u>Epoxy:Fiber Ratio</u>	<u>Surface R</u> <u>(megaohm/sq.)</u>
	A	3.12:1	300
	B	1.26:1	300
10	C	1.31:1	200
	D	1.53:1	200
	E	0.35:1	200
	F	1.50:1	200

15 The stiffness and rate of fuel flow through the battings followed the relative amount of epoxy coating on each batting. Batting A had the greatest stiffness and had the best fuel flow rate whereas Batting E was
20 the softest and had the least stiffness and thus had a higher fuel flow rate. This example also surprisingly shows that the battings retain good antistatic properties over a large coating range of epoxy coating.

25 Example 5

 The batting of Example 4 was processed on a Hunter Fiber Locker to obtain a mechanical bonding by the needle punching process. The resulting structure
30 was suitable as an antistatic, antislosh and flame arresting outer container liner structure in a container for flammable fluids.

Example 6

35 Following the procedure disclosed in European Application Serial No. 0199567, a 6K OPF (i.e., 6000

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filament oxidized polyacrylic fiber) PANOX™ stabilized tow was knit into a plain jersey fabric on a flat bed knitting machine at a rate of 3 stitches/cm and was then heat treated at a temperature of 550°C. The cloth was deknitted and the tow (which had a coil elongation or reversible deflection ratio of greater than 1.2:1) was cut into 7.5 cm length staple. The cut staple was then carded on a Platt Miniature carding machine to produce a wool-like fluff having fibers ranging from 6.5 cm to 7.5 cm in length. The wool-like fluff had a measurable electrical conductivity (a resistance of less than 125K ohms/2.5 cm). A small portion of the resulting fluff (0.14 g) was placed in a 75 ml laboratory widemouthed bottle. No compression was used to place more than the free volume of the fluff into the bottle. The bottle was then approximately 90 percent filled with 55 g of a highly refined liquid hydrocarbon (kerosene) and sealed. The electrical resistance across 2.5 cm of kerosene was greater than 20 megaohms with no fluff present and less than 125K ohms with fluff present (this value of less than 125K ohms across 2.5 cm is well within the antistatic range). The bottle was shaken and inverted several times and trapping of air bubbles and a significant antisloshing effect due to the fluff was observed. During the inversion, the carbonaceous fiber batting was compressed by about 10 percent. The bottle was opened and the kerosene was poured freely from the bottle. This example showed that the fluff structure is free supporting in a container of short head height (about 7.5 cm) and is effective as an antislosh and antistatic structure.

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Example 7

This example was run to show what effect increasing the density of a carbonaceous fiber structure which was lightly coated with an epoxy resin would have on the amount of liquid retained by the structure.

A 0.48 g portion of Sample E from Example 4B (epoxy resin to fiber ratio of 0.35:1) was loaded into a 125 ml bottle and the bottle filled with 100.12 g of kerosene. The bottle was turned upside down and the kerosene was allowed to flow out of the bottle for a period of about 30 seconds. The kerosene which flowed from the bottle weighed 91.65 g. Thus, 8.47 grams were retained in the bottle. A second bottle was filled with 0.99 g of the coated sample and the bottle filled with 96.6 grams of kerosene. The bottle was turned upside down and the kerosene was allowed to run out of the bottle for 30 seconds. 79.71 grams of the kerosene flowed from the bottle. Thus, 16.89 grams or 17.3 percent by weight was retained by the structure in the bottle. This example showed that when the structure is lightly coated with an epoxy resin, an increase in the density of the structure increases the amount of liquid retained by the structure.

Examples 8 and 9

These examples were run to show the effect of stiffness caused by coating the carbonaceous fiber structure versus the fuel flow characteristics.

In a first experiment, 4.63 g of an uncoated carbonaceous fiber batting of Example 4A was placed in a 125 ml widemouthed laboratory bottle to which was

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added 85 g of kerosene. The bottle containing the uncoated structure of the invention was rotated and shaken several times. The bottle was then opened and inverted for 30 seconds, during which time interval
5 1.7 g, or 2 percent, of the kerosene flowed out of the bottle. Approximately 98 percent of the kerosene was retained by the structure.

In a second experiment, 4.63 g of a coated
10 carbonaceous fiber batting of Sample F of Example 4B was placed in the 125 ml widemouthed laboratory bottle to which was added 85.57 g of kerosene. The bottle containing the coated structure of the invention was rotated and shaken several times. The bottle was then
15 opened and inverted for 30 seconds during which time interval 82.46 g, or 95.3 percent, of the kerosene flowed out of the bottle. Less than 5 percent of the kerosene was retained by the stiffened coated
20 structure.

These experiments show that the fuel retention is a function of the stiffness of the structure and not the mass of the structure per se. The uncoated batting
25 would be therefore very useful as an outer liner for a fuel tank to retard spillage of fuel in the case of tank penetration or rupture whereas the coated example would be very useful inside of a fuel tank where antislosh, flame arresting and antistatic properties
30 and good flow rates are required.

Examples 10-13

In another series of examples, the flow rates
35 and antisloshing characteristics of various embodiments of the invention were demonstrated and compared to a

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currently used foam structure. A nominal 15 cm OD PYREX™ (a trademark of Corning Glass Works) glass tube 1.8 m long was sealed at both ends with removable plates having valves fitted in the plates. The tube was suspended at its central portion in a trunnion assembly so that the entire tube could be rocked and/or rotated 360 degrees. This tube was packed with each example of material to be tested for slosh and drain characteristics.

The materials tested in this series of examples were 600 g of standard blue polyether urethane reticulated foam, a 400 g sample of example 4A, and Samples A (275 g), B (356 g), and D (300 g) of Example 4B, the latter four examples containing embodiments of the material of the invention. The sample of Example 4A had no stiffener coating whereas the remaining samples had different amounts of coatings as described in Table I. The tube was filled with 31.5 liters of kerosene and partial drain rates measured. The tube was then rotated 180 degrees to measure the relative antislosh characteristics for each example. "Time 1" in Table II represents the time in seconds for 80 percent of 10.5 liters of kerosene to move from the top to the bottom of the 1.8 m tube whereas "Time 2" represents the time in seconds for 90 percent of the 10.5 liters (33 percent full tank) of kerosene to slosh back from top to bottom after rotation. On a total 31.5 liter drain test Example 13 retained 0.35 liters of fluid or only 1.1 percent fuel retention.

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TABLE II

Example No.	Sample	Fraction Drained	Time (sec)	<u>Slosh Test (sec)</u>	
				<u>Time 1</u>	<u>Time 2</u>
Comparative Sample	Blue Foam	0.33	60	-	-
		0.67	-	60	80
10	4A	0.33	>2000		
	No coating	0.67		>1800	
11	A	0.33	26		
	3.12:1	0.67	71	48	74
12	B	0.33	35		
	1.26:1	0.67	105	102	115
13	C	0.33	32		
	1.53:1	0.66	88	-	-
		1.00	160		

Example 14

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A 6K linear tow of PANOX™ oxidized polyacrylic fiber (OPF) was heat treated at 650°C similar to the heat treatment described in Example 3. This heat set linear fiber tow was cut into 7.5 cm staple length, opened with turbulent air and blended with 75 percent of 6 denier polyester fiber and made into a 2.5 cm thick batting having a bulk density of approximately 9 kg/m³. This batting was then thermally bonded in a Benz hot air oven in a manner similar to that of

Example 3. This material passed the vertical burn test as described in ASTM test procedure 14 CFR 25.853b and had an electrical resistance of less than 1 megaohm/2.5 cm (in the effective antistatic range).

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This material was shown to be effective as a flame retardant material useful as an antislosh, antistatic flame arresting structure.

5 Example 15

 A 6K linear fiber tow of PANOX™ oxidized polyacrylic fiber (OPF) was heat treated at 650°C similar to the heat treatment described in Example 3. This heat set linear tow was cut into 7.5 cm staple length, opened with turbulent air and blended with 60 percent of 6 denier high melting polyester fiber, 15 percent low melting polyester binder fiber, and made into a 2.5 cm thick batting having a density of approximately 9 kg/m³. This batting was then thermally bonded in a Benz hot air oven in a manner similar to that of Example 3, with the exception that the temperature of the oven was set in between the melting points of the regular polyester fiber and the lower melting polyester binder fiber. This allowed only the binder fiber to melt and created a batting with a lower density and higher loft than that made in Example 14. This material passed the vertical burn test as described in 14 CFR 25.853b and had an electrical resistance of less than 1 megaohm per 2.5 cm (in the effective antistatic range). This material was shown to be effective as a flame retardant material useful as an antislosh, antistatic, flame arresting structure.

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 Having described the invention in detail and by reference to the preferred embodiments thereof, it will be apparent that modifications and variations, such as may be readily apparent to persons skilled in the art,

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are intended to be included within the scope of the invention as herein defined in the appended claims.

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1. A flame arresting structure for use with containers for holding flammable fluids comprising a multiplicity of nonflammable, substantially irreversibly heat set, carbonaceous fibers having an
5 LOI value greater than 40, said carbonaceous fibers being present in an amount effective for arresting a flame front.

2. The structure of Claim 1, wherein said
10 carbonaceous fibers are selected from nonlinear fibers or blends of nonlinear and linear fibers in which the linear fibers are present in the blend in an amount of less than 15 percent, based on the total weight of the
15 fibers.

3. The structure of Claim 2, wherein said nonlinear carbonaceous fibers have a sinusoidal or coil-like configuration and a reversible deflection
20 ratio of at least 1.2:1.

4. The structure of Claim 1, 2 or 3, wherein said carbonaceous fibers have an aspect ratio of greater than 10:1 and a nitrogen content of from 16 to
25 25 percent.

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5. The structure of any one of the preceding claims, wherein said carbonaceous fibers are electrically conductive, have a carbon content of greater than 85 percent by weight, an electrical resistance of less than 4×10^3 ohms/cm, and a specific resistivity of less than 10^{-1} ohms/cm.

6. The structure of any one of Claims 1 to 4, wherein said carbonaceous fibers are electrically nonconductive and do not possess any electrostatic dissipating characteristics, said fibers having a carbon content of greater than 65 percent but less than 85 percent by weight, an electrical resistance of greater than 4×10^6 ohms/cm, and a specific resistivity of greater than 10^{-1} ohms/cm.

7. The structure of any one of Claims 1 to 4, wherein said carbonaceous fibers have a low electrical conductivity and electrostatic dissipating characteristics, said fibers having an electrical resistance of from 4×10^6 to 4×10^3 ohms/cm.

8. The structure of any one of the preceding claims, wherein said carbonaceous fiber structure is in the form of a wool-like fluff, webbing, matting or batting comprising a multiplicity of entangled continuous or staple carbonaceous fibers having a bulk density of from 2.4 to 32.0 kg/m³.

9. The structure of any one of the preceding claims, wherein said carbonaceous fiber structure contains an organic or inorganic binder.

10. The structure of any one of Claims 1 to 8, wherein said carbonaceous fiber structure is rigidified by bonding the carbonaceous fibers in the

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structure one to another with a thermoset or thermoplastic polymeric binder to produce a structure having structural integrity and to maintain an open porous structure in the presence of said flammable fluid.

11. The structure of Claim 9 or 10, wherein said carbonaceous fibers contain less than 25 percent by weight of said binder, and said binder is selected from polyester fibers or an epoxy resin.

12. The structure of any one of the preceding claims, wherein said carbonaceous fibers are blended with high performance polymeric fibers.

13. The structure of any one of the preceding claims, wherein said carbonaceous fibers are derived from oxygen stabilized acrylic fibers having a diameter of from 4 to 25 microns.

14. The structure of Claim 13, wherein said acrylic fibers are selected from acrylonitrile homopolymers, acrylonitrile copolymers and acrylonitrile terpolymers, wherein said copolymers and terpolymers contain at least 85 mole percent acrylic units and up to 15 mole percent of one or more monovinyl units copolymerized with another polymer.

15. The structure of any one of the preceding claims, wherein said carbonaceous fiber structure is positioned on the outer surface of the container and is capable of arresting a flame front extending through a rupture in the container.

16. The structure of any one of the preceding claims, wherein said carbonaceous fiber structure is

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positioned on the inside of the container to dissipate the buildup of static electrical energy and to substantially retard sloshing of the liquid within the container.

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17. A container for holding a flammable liquid and/or gas, wherein the inside of said container contains a carbonaceous fiber structure in an amount sufficient to dissipate the buildup of static
10 electricity and to substantially retard sloshing of the liquid within the container but without preventing flow of the flammable liquid from the container, and wherein at least a portion of an outer surface of said
15 container is covered with a flame arresting carbonaceous fiber structure in an amount sufficient to arrest a flame front of the flammable liquid and/or gas from passing through a rupture in the container, said carbonaceous fiber structure comprising a multiplicity
20 of substantially irreversibly heat set, nonflammable, continuous or staple carbonaceous fibers in the form of a wool-like fluff, webbing, matting or batting having a bulk density of from 2.4 to 32 kg/m³.

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18. The container of Claim 17, wherein the carbonaceous fiber structure within the container is provided with a thermoset or thermoplastic polymeric binder to form a web having structural integrity to maintain an open porous structure in the presence of a
30 liquid.

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19. The container of Claim 17, wherein said carbonaceous fibers have an LOI value of greater than 40, and a coil-like and/or sinusoidal shape with a deflection ratio of greater than 1.2:1.

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20. A process for arresting flames in or about a container containing a flammable fuel by providing said container with a fibrous structure comprising a multiplicity of nonflammable,
5 substantially irreversibly heat set, carbonaceous fibers having an LOI value greater than 40.

21. The process of Claim 20, including the step of positioning said fibrous structure within the
10 container to prevent sloshing of the fuel and to dissipate the buildup of an electrostatic charge in the container.

22. The process of Claim 20 or 21, including
15 the step of covering at least a portion of an outer surface of said container with said carbonaceous fiber structure in an amount sufficient to arrest a flame front of the flammable liquid and/or gas from passing
20 through a rupture in the container.

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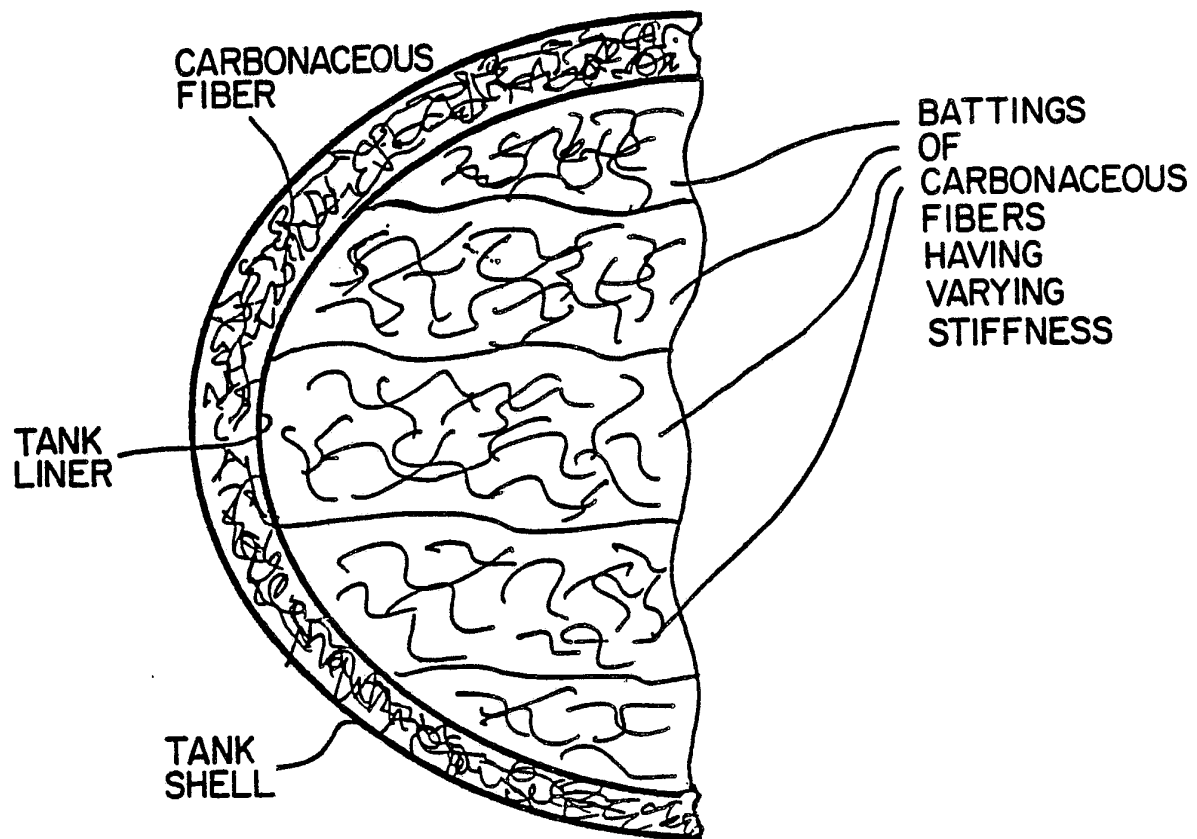


FIG. 1

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US88/03662**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL: (4)B32B 9/00 U.S. CL: 220/85R, 88R; 428/367, 369, 913								
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black; padding: 5px;">Classification System</th> <th style="border: 1px solid black; padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 10px;">U.S.</td> <td style="border: 1px solid black; padding: 10px;">220/85R, 88A, 88R 428/367, 369-371, 408, 913</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	220/85R, 88A, 88R 428/367, 369-371, 408, 913		
Classification System	Classification Symbols							
U.S.	220/85R, 88A, 88R 428/367, 369-371, 408, 913							
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category *</th> <th style="width: 60%; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="vertical-align: top; padding: 10px;">A, P</td> <td style="vertical-align: top; padding: 10px;">US, A, 4,764,408 (STEDMAN) 16 AUGUST 1988</td> <td style="vertical-align: top; padding: 10px;">1-4, 17-22</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A, P	US, A, 4,764,408 (STEDMAN) 16 AUGUST 1988	1-4, 17-22
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<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>								
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 27 JANUARY 1989 </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 07 MAR 1989 </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority ISA/US </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer W. J. VANBALEN </td> </tr> </table>			Date of the Actual Completion of the International Search 27 JANUARY 1989	Date of Mailing of this International Search Report 07 MAR 1989	International Searching Authority ISA/US	Signature of Authorized Officer W. J. VANBALEN		
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International Searching Authority ISA/US	Signature of Authorized Officer W. J. VANBALEN							

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☒ Claim numbers 5-16, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.