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FUEL CELL

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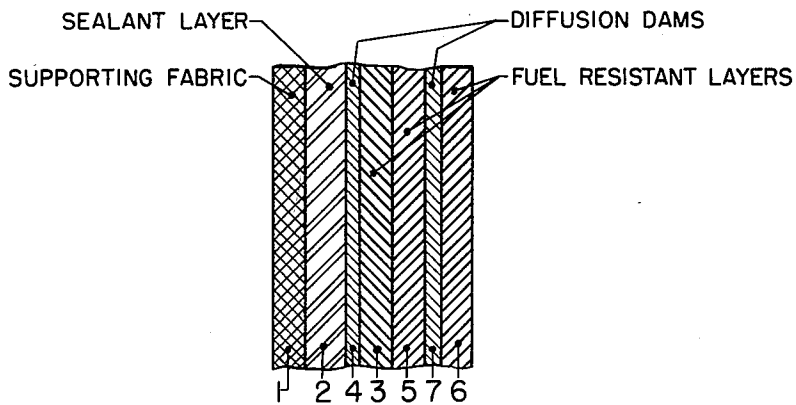


FIG.-1

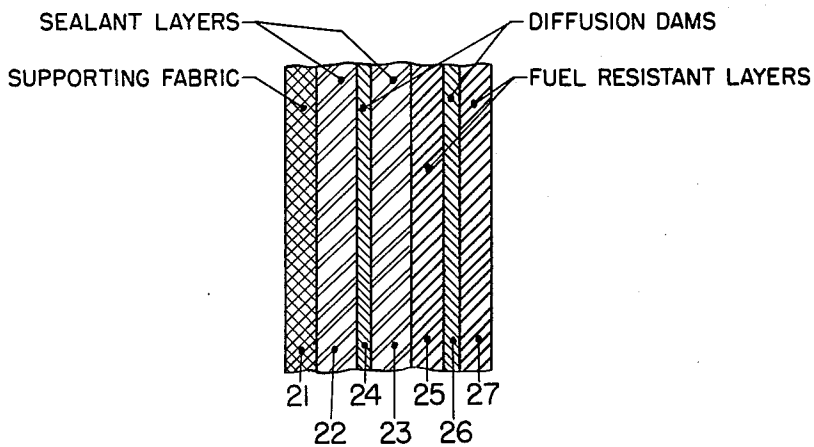


FIG.-2

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FUEL CELL

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4 Claims. (Cl. 154—43.5)

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This invention pertains to the construction of fuel containers, fuel hose and in general to all manner of objects which require a high degree of oil—or hydrocarbon—solvent resistance coupled with a high degree of flexibility at low temperatures.

In the ordinary construction of self-sealing or bullet-proof aviation fuel tanks, flexible fuel cells, fuel hose and the like it has been common practice to employ oil resistant synthetic rubbers as inner liners for all surfaces coming in contact with the fuel. It is essential, of course, that such rubbers possess a high resistance to swelling or deterioration by fuels such as aviation gasoline in order to avoid rapid destruction of the cell and also to avoid contamination of the fuel by extractable matter from the rubbery materials used. It is also essential that the oil or fuel resistant rubbery materials used in such constructions possess a high degree of flexibility at low temperatures because if they lose their flexibility and become brittle at low temperatures, they tend to chunk and shatter when penetrated by a projectile at low temperatures. When large chunks of liner are removed as by the passage of a bullet therethrough, an unduly large area of the sealant layer is exposed, generally causing the cell to fail to seal or causing serious impairment of the usefulness of the cell because of contamination of the fuel.

It is known that rubber-like polymers of good solvent resistance are obtained if a conjugated diolefin such as butadiene, isoprene or piperylene is polymerized in aqueous emulsion with a nitrile of a low molecular weight unsaturated acid such as acrylonitrile, methacrylonitrile or the like in the ratio of about 75 parts of the diolefin to about 25 parts of the nitrile. The copolymer thus formed contains about 25% of combined nitrile. Products of higher oil resistance can be obtained by increasing the ratio of acrylonitrile to diolefin in the reaction mixture so that the content of combined nitrile in the resultant copolymer is 30, 35 or 40% or even higher. Unfortunately, the copolymers of high nitrile content (i. e. containing about 25% or more of combined nitrile) tend to become hard and brittle and possess poorer freeze resistance than those of lower nitrile content. For example, a copolymer of butadiene and acrylonitrile containing 35% of combined nitrile possesses high solvent resistance and easily meets maximum extract specifications and has been used as the liner in bullet-proof aviation fuel tanks. However, as the altitudes at which combat aircraft operate has increased, the requirements

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for low temperature performance of these tanks has become progressively more rigid and more difficult to meet. In view of the inability of the above copolymer containing 35% of combined acrylonitrile to meet the low temperature performance requirements, there has been a tendency recently to switch to lower nitrile polymers in order to retain better flexibility at low temperatures. This has failed to solve the problem, however, since the lower nitrile polymers give rise to a serious problem of contamination of the fuel.

It is the object of this invention to provide the art with a polymer material having high solvent resistance as well as a high degree of flexibility at low temperatures.

It is also the object of this invention to provide the art with a material for the construction of self-sealing fuel tanks, fuel hose and other objects requiring a high degree of solvent resistance as well as a high degree of flexibility at low temperatures.

These and other objects will appear more clearly from the detailed description and claims which follow.

It has now been found that self-sealing fuel tanks, fuel hose and other objects requiring a high degree of solvent resistance as well as a high degree of flexibility at low temperatures may be advantageously fabricated from a laminated material comprising multiple layers of diolefin-acrylonitrile type copolymers of differing nitrile content and in which the polymer of highest solvent resistance and highest nitrile content is placed in immediate contact with the fuel and is backed up by successive thin sheets or layers of copolymer of progressively lower nitrile content and progressively superior low temperature properties. In this way it is possible to produce fuel cells of satisfactory oil resistance and greatly improved low temperature properties.

Reference is made to the accompanying drawing illustrating two embodiments of the present invention. In the drawing, Figure 1 is a cross section of a self-sealing fuel cell having a fuel resistant liner of three layers of diolefin-nitrile copolymer and a single sealant layer, and

Figure 2 is a cross sectional view of another self-sealing fuel cell wherein the fuel resistant inner liner comprises two layers of diolefin-nitrile copolymer and two sealant layers.

The copolymers used in preparing the laminae in accordance with the present invention are obtained by polymerizing a conjugated diolefin such as butadiene, isoprene or piperylene in aqueous

emulsion along with a nitrile of a low molecular weight unsaturated acid such as acrylonitrile, methacrylonitrile and the like. The preparation of such copolymers is described in U. S. Patent No. 1,973,000. The copolymers containing more than about 25% of combined nitrile are preferably prepared by adding the diolefin portionwise during the polymerization as disclosed in application Serial No. 454,754 filed August 14, 1942, by Byron M. Vanderbilt, now U. S. Patent 2,393,206, dated January 15, 1946.

A typical procedure for the preparation of the copolymers which are used in the present invention is as follows:

55.5 parts by weight of butadiene and 19.5 parts by weight of acrylonitrile were dispersed in 200 parts by weight of water to which was added 3.5 weight percent (based on the water) of oleic acid (computed as soap) and 76% of the amount of potassium hydroxide theoretically necessary to convert the oleic acid to potassium oleate. 0.25 weight percent (based on the water) of Lorol mercaptan and 0.6 weight percent (based on the water) of potassium persulfate were added to the mixture whereupon the mixture was maintained under good agitation at 94° F. for 5 hours and at 105° F. for an additional 12 hours. During the run an additional amount of potassium hydroxide equal to 17% of the amount theoretically necessary to convert the oleic acid used to potassium oleate was added to the reaction mixture. After 7½ hours and after the twelfth hour, 0.125 weight percent (based on water) of Lorol mercaptan was added to the mixture. At the end of 17 hours, the latex was stripped of unreacted monomers and coagulated. The polymerization conversion of hydrocarbons amounted to 78%. Lorol mercaptan is prepared from "Lorol" alcohol (Du Pont), a commercial mixture of alcohols containing approximately 55% of C₁₂, 30% of C₁₄ and 15% of C₁₆ alcohols.

If it is desired to reduce the amount of extractables contained in this polymer, that may readily be accomplished by adding about 0.25 to about 1% of caustic soda or other suitable alkali to the coagulate slurry, filtering and washing the coagulate as described in application Serial No. 529,508, filed April 4, 1944, by Harold J. Rose and Joseph L. Betts, now abandoned.

The polymer may then be compounded as desired, generally a moderate amount of loading such as carbon black or other pigment material is added as well as sufficient sulfur and accelerator to effect a moderate degree of curing of the polymer, whereupon the polymer compound may be rolled out into sheets of the desired thickness and cured. In lieu of separately curing the several diolefin-nitrile copolymer sheets of different nitrile content and then laminating them by means of a suitable cement the several sheets of copolymer may be superposed in uncured state and cured as a unit.

Also instead of coagulating the polymer, compounding, sheeting, curing and the like, the several sheets may be prepared by utilizing a latex technique, creaming the polymer latex, if desired adding the desired compounding ingredients and depositing a film of the resultant composition on a belt or the like, converting the latex to the gel form and curing. In this way films of any desired thickness may be readily prepared. Also, by successively changing to latices of polymers of greater or lesser combined nitrile content it is possible to prepare a laminated

structure of any number of layers of copolymer of any desired nitrile content and of any suitable thickness without resorting to the use of adhesives or cements.

In constructing self-sealing fuel tanks, the walls are constructed of several layers of different materials. The innermost layer, i. e. the surface in direct contact with the fuel, is the laminated sheet in accordance with the present invention while the outermost layer is made of some durable, abrasion resistant material. The outer layer may suitably be constructed of leather, plywood, tire cord or the like. The essential requirements that must be met by the material used in this outer layer are that it must be sufficiently firm to render the tank structure substantially self-sustaining and yet not be so hard or brittle as to shatter or tear enlarged holes when pierced by a bullet. Between said inner and outer layers there is provided a sealant layer consisting of a material that swells rapidly when contacted with hydrocarbon fuels. The sealant layer may be prepared from natural rubber or synthetic rubber-like material which have poor or relatively poor solvent resistance such as diolefin hydrocarbon emulsion polymers or emulsion copolymers with styrene or the like or high molecular weight polymers prepared from isoolefins or mixtures of isoolefins and diolefins at temperatures below -10° C. and in the presence of Friedel-Crafts type catalysts.

Two typical bullet-proof or self-sealing fuel cell structures utilizing the present invention are illustrated in the accompanying drawing.

The cell shown in Figure 1 comprises an outer supporting fabric layer 1 which may be made from tire cord and a sealant layer 2 which may be made of natural rubber, butadiene-styrene copolymer, emulsion polybutadiene, polysobutylene or the like. The sealant layer 2 is secured to an oil-resistant layer 3 by means of a suitable cement 4. Premature swelling of the sealant layer may be prevented or minimized by utilizing a nylon cement which, being unaffected by hydrocarbon motor fuels, forms a diffusion dam. The oil-resistant layer 3 may desirably be formed from a butadiene-acrylonitrile copolymer containing a relatively low amount of combined nitrile, for example, from about 10 to 20% of combined nitrile and is secured to a second oil-resistant layer 5 having a higher content of combined nitrile, i. e., 20-30%. The innermost oil-resistant layer having the highest oil or solvent resistance is made of a butadiene acrylonitrile copolymer containing from about 30 to 40% of combined nitrile and is preferably secured to the layer 5 by means of nylon cement which forms a dam 7 preventing or minimizing the diffusion of fuel through the cell wall. A cell wall made of three plies of butadiene-acrylonitrile copolymer containing 18%, 26% and 35% of combined nitrile, corresponding to the layers 3, 5 and 6 respectively of Figure 1 were prepared and subjected to shooting tests at -20 and -40° F., in one case the slab being shot so that the bullet entered through the layer of lowest nitrile content and in the other so that the bullet entered through the layer of highest nitrile content. The results obtained were substantially the same regardless of the direction in which the bullet entered. At -20° C. one shot entering the 35% nitrile content layer chunked the topmost layer, the other layers having a mere pin hole or at most a short tear in it. At -10° C. well as at -20° F. a slab made up of the 35% com-

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bined nitrile polymer only had a hole about half the size of the bullet chunked out of it. At -40° F. all three layers of the slab were chunked by the bullet, the largest holes, occurring in the layer containing 35% combined nitrile, being slightly smaller than the holes formed in the slab made of 35% nitrile copolymer at -40° F., the other holes being progressively smaller as the nitrile content decreases. This makes for a marked advantage in bullet-proof or self-sealing fuel cells since it decreases the strain placed on the sealant layer.

The cell structure shown in Figure 2 comprises two sealant layers as well as two fuel-resistant layers. The outermost layer is, as in Figure 1a, supporting fabric layer 21 of tire cord or the like. The two sealant layers 22 and 23 may be made of the same or different swellable rubbery materials such as natural rubber, butadiene-styrene copolymer, emulsion polybutadiene, polyisobutylene or the like or mixtures of such materials. The two sealant layers are adhered together by means of nylon cement, for example, forming a diffusion dam 24. The fuel-resistant layers comprise a layer 25 adhered by means of nylon cement layer 26 to the layer 27. The oil-resistant layers 25 and 27 are desirably prepared from butadiene-acrylonitrile emulsion copolymers containing about 26% and about 35% of combined nitrile respectively. This also gives a fuel cell structure that is capable of withstanding penetration by bullets and the like at lower temperatures than a similar fuel cell having only one fuel-resistant layer of butadiene-acrylonitrile copolymer containing 35% of combined nitrile.

It may thus be seen that in accordance with the present invention, fuel cells are rendered capable of self-sealing at much lower temperatures since the laminated fuel-resistant liners combine the high fuel resistance characteristics of high combined nitrile content copolymers with the flexibility and resistance to chunking and shattering at low temperature of the lower combined nitrile content copolymers.

The foregoing description contains a limited number of embodiments of the present invention but it will be understood that my invention is by no means limited to the specific details described since numerous variations are possible without departing from the scope of the following claims.

What I claim and desire to secure by Letters Patent is:

1. A self-sealing liquid hydrocarbon fuel container, the walls of which comprise an outer layer of durable abrasion-resistant material, on the inner side thereof a sealant layer comprising essentially a rubber-like material adapted to swell on contact with a hydrocarbon liquid fuel, said sealant layer comprising at least one-ply of material selected from the class consisting of natural rubber, butadiene-styrene synthetic rubber, polybutadiene synthetic rubber, high molecular weight

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polymerized olefins and high molecular weight iso-olefin-diolefin copolymers, and on the inside of said sealant layer a fuel-resistant layer comprising a plurality of laminae made of fuel-resistant rubber compositions the rubbery constituents of which consist of copolymers of a conjugated diolefin and a nitrile of a low molecular weight unsaturated acid, the nitrile content of said copolymers ranging from 10 to 40% by weight, and the nitrile content of the copolymer in the innermost lamina being substantially greater than the nitrile content of the copolymer in the fuel-resistant lamina immediately adjacent to the sealant layer, the said layers being bonded together to produce a laminated fuel-resistant wall construction having high fuel-resistance characteristics yet good flexibility and resistance to chunking and shattering at low temperature.

2. Container according to claim 1 in which the nitrile content of the copolymer in the innermost lamina of the fuel-resistant layer is 30 to 40%, and the nitrile content of the copolymer in the fuel-resistant lamina adjacent to the sealant layer is 10 to 20%.

3. Container according to claim 1 in which the fuel-resistant layer comprises three laminae of emulsion copolymerizates of butadiene-acrylonitrile containing 10-20%, 20-30%, and 30-40% respectively of combined nitrile progressively from the lamina adjacent to the sealant to the innermost lamina which is subject to contact with liquid hydrocarbon fuel when present in the container.

4. Container according to claim 3 in which the copolymers in the fuel-resistant laminae contain 18%, 26% and 35% respectively of combined nitrile progressively from the lamina adjacent to the sealant to the innermost lamina.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,297,305	Thacher	Mar. 11, 1919
1,779,397	Kraft	Oct. 21, 1930
1,931,922	Damsel et al.	Oct. 24, 1933
2,227,900	Habgood et al.	Jan. 7, 1941
2,271,125	Juve	Jan. 27, 1942
2,278,802	Sarbach	Apr. 7, 1942
2,381,739	Gray	Aug. 7, 1945
2,405,986	Sullivan	Aug. 20, 1946
2,406,679	Gray et al.	Aug. 27, 1946
2,430,931	Hershberger	Nov. 18, 1947

OTHER REFERENCES

"Perbunan properties and compounding," by Moll, Howlett and Buckley, in *Industrial and Engineering Chemistry* for Nov. 1942, page 1291.