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W. C. SMITH ET AL
PUNCTURE-PROOF FUEL CELL
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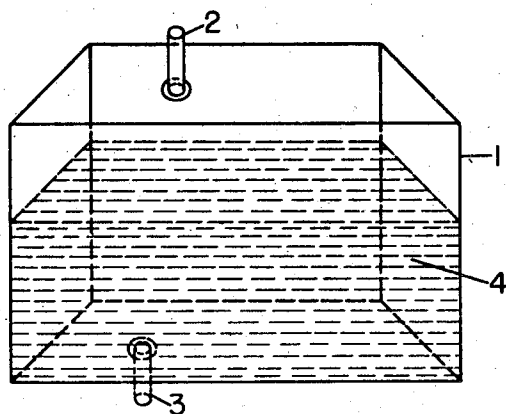


FIG.-1

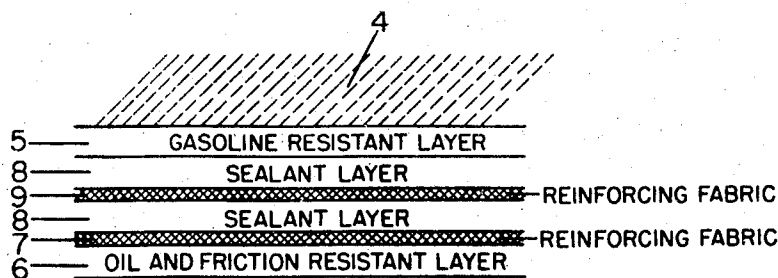


FIG.-2

Joseph P. Haworth
Winthrop C. Smith INVENTORS
BY *R. Young* ATTORNEY

UNITED STATES PATENT OFFICE

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PUNCTUREPROOF FUEL CELL

Winthrop C. Smith, Elizabeth, and Joseph P. Haworth, Westfield, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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12 Claims. (Cl. 154—43.5)

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This invention relates to fuel containers, relates particularly to gasoline tanks for airplanes; and relates especially to the swellant layer in puncture-proof airplane gasoline tanks; and to means for maintaining the puncture-proof properties of the tanks even at temperatures below zero.

Airplane gasoline tanks, especially on military and combat planes, consists of cells prepared from fabric and rubbery materials which are fitted into appropriate locations in the plane, usually in the wings. Each cell consists of a gasoline-resistant inner liner to hold the fuel; and an outer layer of reinforcing structure consisting of a heavy fabric coated on the outside with oil-resistant abrasive-resistant rubbery compound to protect the cell against oil, fuel or friction which might injure the cell when stowed away in the wing of the plane. Between the inner gasoline-resistant liner, and the outer protective layer, there is placed a swellable sealing compound, usually reinforced by additional fabric. A bullet or other bit of metal driven through the wall of the cell will make a hole through which the fuel can leak. However, the interposed layer of swellable compound absorbs gasoline and swells sufficiently from the absorbed gasoline to close the hole.

In the past, a layer of poly-chloroprene or of the interpolmer of butadiene and acrylonitrile has been used as the inner liner; and a layer of similar material, reinforced with fabric has been used for the outer layer; with a layer of natural rubber, reinforced with fabric for the interposed swellable layer. However, the unavailability of natural rubber has made it necessary to find a substitute for natural rubber. Such compounds as poly-chloroprene and the interpolmer of butadiene and acrylonitrile do not swell in the presence of gasoline; and while the interpolmer of butadiene and styrene shows much better swelling properties, it is difficult to fabricate it into a fuel cell under proper conditions for utilizing the swelling; furthermore, of the other available elastic, plastic substances, only the low temperature interpolmer of isobutylene with a diolefin shows sufficient strength, sufficient ease of fabrication, and sufficiently rapid swelling properties to be a satisfactory swellant layer. However, this polymer shows a poor freeze resistance, and at temperatures below about 0° C., it becomes so stiff that the passage of a bullet through it results in a shattering of the fuel cell so great that the polymer can not swell sufficiently to close the hole.

Thus the present invention provides a synthetic sealing member for use interposed between the

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gasoline-resistant inner layer and the oil-resistant outer layer which is swellable rapidly by gasoline over a temperature range from 125° F. to -60° F. without becoming sufficiently stiff to shatter under the impact of a rifle bullet.

According to the present invention, there is used for fuel cells the inner sealing layer of poly-chloroprene or the polymer of butadiene and acrylonitrile, and the outer layer of fabric coated with oil-resistant, abrasive-resistant material; with an interposed layer of the low temperature interpolmer of isobutylene with a diolefin which is compounded with a substantial proportion of a highly paraffinic hydrocarbon oil having a boiling point within the range between 200° F. and 700° F. This paraffinic hydrocarbon oil improves the shatter-resistance of the interposed swellable layer at all temperatures over the range from 125° F. to -60° F. without reducing its swellability and without noticeable change of its tensile strength, elongation and other important properties.

Thus the structure of the invention provides a new airplane fuel tank which is resistant to leakage from puncturing by bullets at temperatures ranging from +125° F. to -60° F. without the use of natural rubber. Other objects and details of the invention will be apparent from the following description when read in connection with the accompanying drawing wherein

Fig. 1 is a view in elevation, partly in section, of an airplane fuel cell, and

Fig. 2 is a sectional view of the successive layers of the body of which the fuel cell is constructed.

Referring to the figures, the fuel cell 1 with filler fittings 2 and outlet fittings 3 contains a substantial quantity of gasoline fuel 4. The body of the fuel cell is formed with an inner layer 5 which is gasoline-resistant and preferably consists of a lamina of butadiene acrylonitrile compounded with the usual compounding agents including carbon black, zinc oxide, etc. A suitable recipe is as follows:

Recipe #1

	Parts
Butadiene acrylonitrile copolymer.....	100
Carbon black.....	75
Zinc oxide.....	5
Stearic acid.....	1
Sulfur.....	1.5
Benzothiazyl disulfide.....	1.0
Dibutyl phthalate.....	20.0

Alternatively, the layer 5 may consist of the interpolmer of polychloroprene compounded

with the usual components such as are shown in the following recipe which is representative of suitable compounding recipes:

Recipe #2

	Parts
Polychloroprene.....	100
Carbon black.....	50
Zinc oxide.....	5
Stearic acid.....	1
Extra light calcined magnesia.....	4.0
Dibutyl phthalate.....	5.0

Either of these recipes is conveniently prepared on the open roll mill in the usual manner and is sheeted out on the calender as usual. This layer serves as the inner lining of the fuel cell and it is highly resistant to swelling or penetration by the gasoline fuel. An outer, protective, layer 6 is likewise provided which may be any convenient rubber-like material, but is preferably one of the butadiene polymers which is resistant to oil and friction both. The copolymer of butadiene and acrylonitrile is particularly satisfactory for this outer layer and it may be prepared according to the recipe above given and sheeted out on the calender. A layer of fabric 7 is likewise provided for strengthening and reinforcing purposes; the outer layer 6 being preferably calendered onto the fabric 7. Between the layers 5 and 6 there is provided a swellant or sealant layer 8 having a second layer of fabric 9 incorporated into the swellant layer.

The swellant layer preferably consists of an interpolymer of an isoolefin such as isobutylene with a polyolefin such as butadiene or isoprene or the like, prepared by a Friedel-Crafts catalyst polymerization at low temperature. This sealant layer is compounded with appropriate substances for improving the tensile strength, for curing; and the like; and, in addition, it contains a substantial portion of a moderately heavy hydrocarbon oil to produce resistance to shattering when shot at low temperatures.

In preparing the swellant layer, the components preferably consist of isobutylene as a first component, although other isoolefins such as 2, methyl butene-1, or 2, methyl pentene-1, or 2, methyl hexene-1 may, under some circumstances, be used. The second component of the mixture is a polyolefin such as butadiene or isoprene or piperylene or dimethyl butadiene, or dimethylallyl or myrcene, or the like; substantially any of the polyolefins having from 4 to 12 or 14 carbon atoms per molecule being usable.

In preparing the copolymer of these materials, the olefinic substances are mixed, preferably with a major proportion of the isoolefin and a minor proportion of the polyolefin, superior results being obtained with from 70 to 99.5 parts of isobutylene in the admixture with from 30 to 0.5 of the polyolefin.

This olefinic material is cooled to a temperature within the range of -20° to -100° C. or even lower, down to -165° C., by the use of an appropriate refrigerant. The refrigerant may be used in a refrigerating jacket applied to the reactor or may be admixed directly with the polymerizable olefins. In the latter instance, such substances as liquid propane, liquid ethane, liquid ethylene and even liquid methane are usable, as well as solid or liquid carbon dioxide. When the refrigerant is used in a refrigerating jacket, practically any of the low boiling substances such as the refrigerants above-mentioned, and, in addition, substances such as sulfur dioxide under reduced pres-

sure, or methyl chloride under reduced pressure, or liquid carbon dioxide or other substances under normal atmospheric pressure or reduced pressure or elevated pressure are suitable.

When the olefinic mixture has reached the desired low temperature, it is polymerized by the application thereto of a Friedel-Crafts type polymerization catalyst. This catalyst is preferably aluminum chloride in solution in a low-freezing, non-complex-forming solvent such as ethyl or methyl chloride or the like. For the Friedel-Crafts type catalyst, substantially any of the Friedel-Crafts catalyst disclosed by N. O. Calloway in his article on "The Friedel-Crafts synthesis" printed in the issue of "Chemical Reviews" published for the American Chemical Society at Baltimore in 1935 in vol. XVII, No. 3, pages 327-375 may be used as a catalyst. For the catalyst solvent, substantially any of the mono or polyalkyl halides which have freezing points below 0° C. may be used, these being identified as "low freezing" because they freeze at temperatures below room temperature, all of them being characterized by their freedom from any tendency to form complexes or addition compounds with a metal halide.

The catalyst solution is dispersed as rapidly as possible into the cold olefinic material; preferably by application in the form of a fine spray to the surface of the rapidly stirred, cold, olefinic mixture. Alternatively, however, the catalyst solution may be delivered as a jet into a zone of high turbulence such as forms behind the blades of a stirrer and by other means which will be obvious to those skilled in the art, the principal requirement being rapid dispersion of the catalyst into the olefinic mixture. The polymerization is preferably halted short of the complete polymerization of all of the olefinic material present. This may be accomplished merely by suspending the delivery of catalyst solution; or the polymerization mixture may be dumped into a catalyst-quenching agent such as warm water or warm alkaline solution or warm alcohol solution or the like. In any event, the solid polymer is brought up to room temperature and purified, if desired, by washing on the roll mill or in the kneader or by other convenient means. This polymer is a basic material for the tank swellant member.

The polymer as prepared, can be conveniently compounded according to the following recipe:

Recipe #3

Copolymer	1	2	3
	Parts by weight	Parts by weight	Parts by weight
Copolymer.....	100	100	100-0
Zinc oxide.....	5	5	5
Stearic acid.....	1.5	1.5	1.5
Tuads (tetramethyl thiuram disulfide).....	1.0	1.0	1.0
Mercaptobenzothiazole captax.....	0.5	0.5	0.5
Sulfur.....	1.5	1.5	1.5
Paraffinic oil.....	20-60	20-60	20-60
Gastex (carbon black).....	54		54-0
Prepared copolymer.....			0-100

The above recipes are representative, and may be varied both in proportions and in components in many ways which will be obvious to those skilled in the art without departing from the inventive concept here disclosed.

The hydrocarbon oil, the presence of which in this recipe is of the essence of the invention, is preferably a paraffinic type petroleum oil having a boiling point preferably between about 300° C.

and 500° F. It is desirable that this oil be one which has been highly purified by a treatment with fuming sulfuric acid; but such treatment is not essential to the invention, since a simple distillation cut boiling within this range, taken from a paraffinic oil, is satisfactorily usable. That is, purified paraffinic oils having boiling points between 200° F. and 700° F. are desirable; and paraffinic oils without acid treatment having the same boiling range, such as kerosene, are also usable, satisfactory and effective, although they do not give quite as good results as the purified oils.

The presence of the purified paraffinic oil yields the new and unexpected result that the resulting compound remains elastic at temperatures as low as -60° F., or even lower, without reducing its swelling properties in the presence of gasoline, and without substantial reduction in tensile strength and other physical properties of the polymer.

The precured copolymer listed in the above formula is prepared by compounding the copolymer of isobutylene and a polyolefin, with a curing agent which may be sulfur, or sulfur with a curing aid such as tetramethyl thiuram disulfide, and the like, cured by an appropriate heat treatment and re-plasticized on a cold roll mill. The presence of the precured copolymer is of substantial advantage in factory processing because of the fact that the presence of relatively large amounts of the purified paraffinic hydrocarbon oil causes the stock to become very soft and flowable under its own weight. The presence in the mixture of precured and re-plasticized polymer increases the stiffness and physical strength of the composition to such an extent that it is more easily handled on the mill and in the course of the assembly of the fuel cells. The presence of the precured copolymer does not reduce the physical strength of the cured material, does not reduce the shatter resistance at low temperatures and in some instances, substantially increases the physical strength of the compound. Also the presence of the precured polymer somewhat improves the adhesion between the gasoline-resistant layer and the swellant layer and between the oil and friction-resistant layer and the swellant layer.

In some instances, the several layers may be assembled and cured together with sufficient adhesion between them for the production of a satisfactory fuel cell; especially if the precured polymer is included in the compounding recipe. In other instances, especially when none of the precured polymer is included in the swellant layer, a tie ply is advantageous between the several layers. This tie ply may conveniently consist of a mixture of the materials used for the outer layers with precured and re-plasticized copolymer. For this purpose the raw copolymer is desirably compounded with curing agents such as sulfur, or sulfur with a sulfurization aid, or with para quinone dioxime or its esters, or para dinitroso cymentene or its analogs or homologs or esters. With the latter curing agent, the compounding may be conducted on a cool mill, and the curing and re-plasticizing conducted simultaneously on the same mill at a higher temperature, in view of the very rapid curing effect of the nitroso curing agents.

When the curing is complete, the desired second component such as polychloroprene or the copolymer of butadiene with acrylonitrile may be milled into the replasticized copolymer and the

material sheeted out and interposed between the main layers during the course of the preparation of the fuel cell. Alternatively, the material of the tie ply may be prepared in solution, the necessary curing agents being dissolved in the solution, and the main laminae are then treated on their surfaces with the solution, the solvent evaporated and the laminae placed together in the desired structure.

To indicate the difficulties encountered in the preparation of fuel cells for service at extremely low stratosphere temperatures, a fuel cell was prepared, as shown in Fig. 1, the inner layer of which consisted of a lamina of the butadiene-acrylonitrile copolymer compounded according to Recipe #1 and cured as indicated. The intermediate layer consisted of a polymer of isobutylene and isoprene prepared as above described, compounded according to item 1 of Recipe #3, but without the paraffinic oil. This compound was prepared on the roll mill and calendered onto both sides of the fabric 9. An outer layer for the fuel cell was prepared according to recipe #1, calendered onto the fabric 7 and a skim coating of the same compound was applied to the inner side of the fabric 7. These several laminae were assembled with the aid of the previously described tie ply cements into a fuel cell and placed in the mold. The assembled cell was then cured under heat and pressure for the appropriate length of time, and then removed from the mold.

The cell was then filled nearly full of aviation gasoline, the cell and its contents cooled to -50° C., and a .45 calibre rifle bullet was fired into the cell at point blank range at the low temperature. In the absence of the paraffinic oil in the sealant layer, all of the lamina including this sealant or swellant layer shattered, leaving a large hole in the fuel cell which could not be closed by swelling of the sealant layer, with the consequence that considerable quantities of gasoline were lost from the cell under conditions which, if they had occurred in the airplane, would result in a very severe fire hazard.

Example 1

A similar fuel cell was prepared utilizing an inner lamina of butadiene-acrylonitrile compounded according to Recipe #1; an intermediate lamina of the copolymer of isobutylene and isoprene prepared as above described and compounded according to item 1 of Recipe #3, using 30 parts of the hydrocarbon oil and calendered onto fabric 9 as before, with an outer layer of the same butadiene-acrylonitrile compound calendered onto fabric as before. These several laminae were assembled into a cell, as above pointed out, cured and stripped from the mold.

The cell was then filled with aviation gasoline, cooled to -60° F. and several .45 calibre rifle bullets were fired into the cell at point blank range. In each instance, the sealant layer was found to be resistant to shattering, resulting in the production of only a small hole in which the swelling effect of the gasoline in the cell upon the exposed sealant layer caused an immediate closing of the hole. The sealing of the tank was sufficiently rapid to allow only a momentary dampness of gasoline on the outside of the tank at the entrance and exit points of each bullet. No substantial loss of gasoline occurred and no fire hazard was produced. The same tank and its contents were then warmed to approximately +125° F. and a second series of .45 calibre rifle

bullets were fired through the tank. At this temperature also, immediate sealing of the punctures resulted and no more gasoline was lost from the tank than had occurred at the low temperature.

The tank and its contents were then again cooled to -60°C . and a third series of .45 calibre rifle bullets were fired through the tank. In this instance also, prompt and effective sealing occurred, negligible quantities, amounting only to a momentary dampness being found outside of the cell.

These tests show the efficacy of the sealing action at any temperature between -60°F . and $+125^{\circ}\text{F}$. when the sealant layer contained incorporated hydrocarbon oil as in Recipe #3.

Reports from combat areas further indicate that this effective sealing action is maintained under combat conditions.

Example 2

A similar fuel cell was prepared utilizing for the inner layer the poly-chloroprene compound of Recipe #2, utilizing for the swellant layer item 3 of Recipe #3 with 30 parts of oil, calendered onto fabric 9 with an outer layer of poly-chloroprene compounded according to Recipe #3 and calendered onto the fabric 7. These laminae were particularly easy to assemble because of the presence in the swellant layer of the precured polymer which simplified the assembly problems and yielded a tougher, more durable cell.

Rifle tests, made as described in Example 1, showed an equally high sealing action, and no perceptible difference in leakage of gasoline was found at any temperature as between the two fuel cells of Example 2 and Example 1.

The presence of the precured polymer in the laminae of this cell greatly improved the handling, since the amount of hydrocarbon oil present is sufficiently great to make the polymer layer member soft and plastic with a low stock strength, and high deformation under slight tensions. The presence of the precured copolymer sufficiently strengthens the compound to reduce the deformability very greatly, increase the strength and simplify very greatly the milling, sheeting, calendering and assembling. Also the presence of the precured polymer does not in any way reduce the speed or amount of swelling of the polymer either at low or high temperatures.

Example 3

A series of similar fuel cells were prepared utilizing various other arrangements of the several compositions here shown. One of these utilized an inner lamina of poly-chloroprene, an outer lamina of the interpolmer of butadiene and acrylonitrile and a middle layer of the isobutylene-isoprene interpolmer, all according to Recipes 1, 2 and 3, above set out; the isobutylene-isoprene low-temperature polymer recipe having approximately 30 parts of kerosene incorporated, but without either carbon black or precured copolymer. This cell proved to be somewhat difficult to fabricate because of the fragile character of the middle lamina. However, by careful work a fully satisfactory cell was obtained which, upon testing at temperatures between -60°F . and $+125^{\circ}\text{F}$. as above indicated, showed fully adequate and satisfactory sealing when .45 calibre bullets were fired through the cell.

Another cell was prepared using poly-chloroprene for the inner layer and the copolymer of butadiene and acrylonitrile for the outer layer

with a middle layer according to Recipe 3 using item 3 containing both carbon black and precured copolymer; with approximately 20 parts of acid purified hydrocarbon oil; specifically, acid purified kerosene. This combination of laminae, prepared, as above outlined, proved to be particularly easy to assemble because of the noticeably higher strength of the middle layer because of the presence of the precured copolymer and carbon black, and the smaller quantity of oil. Upon firing tests, this combination also sealed entirely satisfactorily, although there was some possibility of a fraction of a second slower action.

Other combinations of these several polymers also were tried using various combinations of the several outer and inner layer recipes with the several items of Recipe #3 for the copolymer, and it was found that considerable latitude of construction was available without sacrifice of efficiency or effectiveness of sealing. Approximately the minimum amount of the purified paraffinic hydrocarbon which would give immediate sealing and no shattering at -60°F . was about 20 parts of oil per 100 parts of polymer. However, where the minimum temperature to be encountered was only -20°F . to -30°F ., amounts of oil as small as 5-10% would give sufficient resistance to shattering to make the cell satisfactory under these milder temperature extremes; and accordingly, it appears that the minimum significant amount is probably two or three parts of hydrocarbon oil per 100 of polymer for moderately low temperature service. At the other extreme, amounts of hydrocarbon oil as high as 50 or 60 parts per 100 of polymer are usable and prevent shatter at temperatures as low as may be desired. It is, however, somewhat difficult to construct the cells from material containing such high proportions of paraffinic oil. It is found, however, that by very careful handling, the use of substantial quantities of precured copolymer and substantial quantities of filler, amounts of oil up to about 75 parts per 100 of raw polymer can be used. Above these values the difficulty of handling becomes so great as to be commercially unfeasible, although for special service where cost and difficulty of assembly are not factors, somewhat higher amounts can be used.

Thus the invention consists of a fuel cell having outer and inner oil-and-gasoline-resistant laminae and an interposed swellant lamina consisting of a copolymer of isobutylene with a polyolefin containing dissolved therein a purified paraffinic hydrocarbon oil; the resulting fuel cell showing highly satisfactory, effective, and efficient sealing action against punctures at temperatures from $+100$ to $+125^{\circ}\text{F}$. down to temperatures as low as -60°F .

While there are above disclosed but a limited number of embodiments of the invention, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed and it is, therefore, desired that only such limitations be imposed upon the appended claims as are stated therein.

The invention claimed is:

1. A fuel cell comprising a plurality of lamina layers, one thereof being an inner layer of plastic, elastic, gasoline-resistant material, another thereof being an outer layer of plastic, elastic, oil-resistant, abrasion-resistant material and an interposed lamina comprising a cured polymer of isobutylene with a diolefin containing therein a purified paraffinic hydrocarbon oil.

2. A fuel cell comprising a plurality of lamina

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+125° F., the several layers having compounded thereinto carbon black, zinc oxide and stearic acid, the interposed polymer also having precured and replasticized polymer compounded thereinto.

12. A fuel cell comprising a plurality of lamina layers, one thereof being an inner layer of plastic, elastic, gasoline-resistant material, another thereof being an outer layer of plastic, elastic, oil-resistant, abrasion-resistant material having a layer of reinforcing fabric therein and an interposed lamina comprising a cured polymer of isobutylene with a diolefin containing therein a purified paraffinic hydrocarbon oil, the combination being characterized by the capability of holding gasoline, the property of swelling when punctured to prevent leakage of gasoline, and the property of swelling to prevent leakage of gaso-

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line at any temperature between -60° F. and +125° F., the several layers having compounded thereinto carbon black, zinc oxide and stearic acid, the several laminae being held together by a tie ply.

WINTHROPE C. SMITH.
JOSEPH P. HAWORTH.

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