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SELF-SEALING CONTAINER FOR HYDROCARBON FUELS

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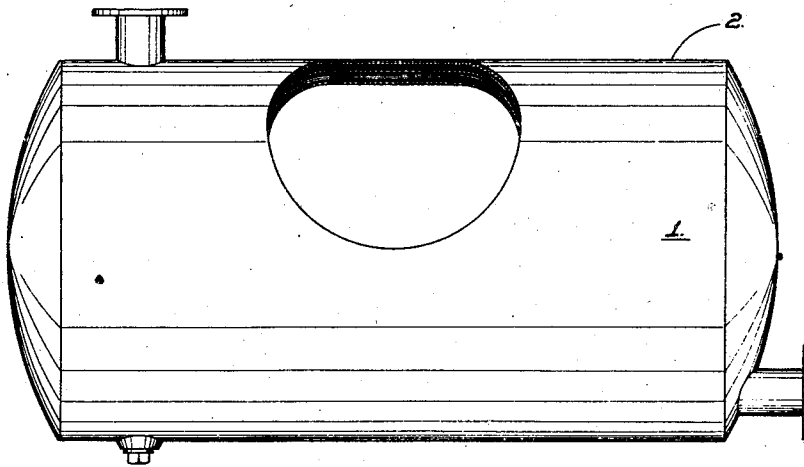


Fig. 1.

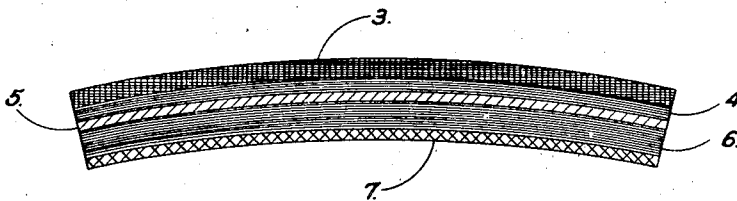


Fig. 2.

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SELF-SEALING CONTAINER FOR HYDRO-CARBON FUELS

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This invention relates to containers having a novel inner liner especially in combination with walls having a self-sealing structure capable of sealing a hole made therein as by such a projectile as a bullet, and more particularly pertains to a self-sealing gasoline tank, especially suitable for a military airplane, having a novel inner liner in combination with the self-sealing means.

The construction of such a container or tank as one suitable for a military airplane, for example, which will be not only self-sealing when punctured or traversed as by such a projectile as a bullet but also otherwise satisfactory as a tank for such motor fuel as gasoline has long presented a very difficult problem. When a high velocity bullet passes through a tank containing a liquid such as gasoline, a pressure wave is set up in the liquid ahead of the bullet passing through it creating a liquid hammer or ram effect against the opposite wall of the tank from which the bullet entered. The result of this effect is a tendency to tear out a large hole where the bullet leaves the tank. This creates a special problem in constructing a self-sealing tank subject to being traversed or punctured by a bullet, since, in addition to overcoming the tendency described above, such a tank must also be otherwise satisfactory for the purpose intended.

The kind of a container to which this invention particularly relates is a self-sealing gasoline tank, which may, for example, have walls comprising, from the outside toward the inside, a layer of very heavy hide leather, a layer of latex approximately $\frac{1}{8}$ inch thick, a layer of sponge rubber about $\frac{1}{4}$ inch thick, another layer of latex about $\frac{1}{8}$ inch thick, a layer of split hide, and an inner liner which is contacted by the gasoline. The inner line serves to retain or hold the gasoline, and the other layers serve as a support and as a self-sealing means when the wall is traversed by a bullet. When a bullet passes through such a wall properly constructed in accordance with this invention, it appears that the sponge rubber tends to push into the hole to prevent substantial leakage of the gasoline, while the latex, when contacted by the gasoline, swells and expands to effect a sealing of the hole. The leather and hide impart strength and some rigidity to the tank wall.

The requirements for a satisfactory inner liner for such a container are numerous and exacting. Such a liner must not only cooperate with the self-sealing means in its function but also must serve as a satisfactory retainer for the contents, such as gasoline, of the container. Among the

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chief disadvantages of prior art materials used for inner liners of containers of the kind referred to above are that such material was subject to corrosion, or was deteriorated by the substances such as gasoline placed in the container, that the material would allow gasoline to be diffused therethrough to the outer layers of the tank wall at an undesirably high rate, that the material would permit extraction of substances by the contents of the container which would contaminate the contents rendering them unsuitable for the purpose intended, gasoline, for example, might be contaminated so as to be harmful to the motor when used as motor fuel, that when traversed by a bullet the liner would be shattered, thus exposing the outer layers of the tank walls to the contents of the tank, or that the material of the liner after being traversed by the bullet, especially from the inside toward the outside accompanied by the liquid hammer or ram effect, would be expanded or torn out in such a way as to hold open the hole left by the bullet by expanded protruded portions extending into the hole so that the self-sealing means could not function properly. Although one kind of a material might be more or less satisfactory so far as many of the requirements are concerned, it would nevertheless have sufficient disadvantage to render the container highly unsatisfactory in some particular respect. For example, even though a thin sheet of aluminum might be more or less satisfactory so far as many of the requirements are concerned, it has the outstanding disadvantage that the liquid ram effect, referred to above, usually leaves a large hole torn in the sheet with portions protruding into the hole preventing the functioning of the self-sealing means. Moreover, other materials, for example, numerous synthetic materials, even though satisfactory to some extent with regard to one or some of the requirements, are unsatisfactory as to other important factors.

It is an object of this invention to provide a self-sealing container which avoids the foregoing disadvantages.

It is a further object of this invention to provide a self-sealing container having a novel inner liner in combination with the outer wall structure including the self-sealing means which improves the container.

Another object of this invention is to provide an improved self-sealing motor fuel tank especially suitable for military airplanes subject to puncture by such a projectile as a bullet.

Further and important objects of this inven-

tion will be apparent from the description which follows.

According to the present invention the significant discovery has been made that polyvinyl acetal resins, especially when modified as herein described, give surprising satisfactory results when used in making the inner liner of such a container having a self-sealing wall structure, especially a container or tank for such hydrocarbons as gasoline, benzene, lubricating oil, etc. The polyvinyl acetal resins described in U. S. Letters Patent to Morrison et al., Reissue No. 20,430, issued June 29, 1937, and in French Patent No. 793,175 exemplify resins suitable for the purpose of this invention. These resinous compositions are tough, elastic and flexible, and an inner liner made in accordance with this invention cooperates with the rest of the wall structure, including the self-sealing means, to produce remarkably improved results in a self-sealing container, especially a gasoline tank for a military airplane, for example.

The liners made in accordance with this invention do not corrode, as metals, for example, are resistant to deterioration by water or such contents as hydrocarbons including gasoline, benzene, lubricating oils, etc., have a surprisingly low average rate of diffusion therethrough by such materials as gasoline, do not permit extraction of substances by hydrocarbons which would contaminate the contents of the container, especially such hydrocarbons as gasoline, benzene, lubricating oil, for example, are tough, elastic and flexible and cooperate with the outer wall layers, which include the self-sealing means, to make it possible to make a wall such that, even a high speed bullet passing through the liquid contents and out through the wall accompanied by the liquid hammer or ram effect, produces only such a hole as can readily be sealed by the self-sealing means.

In order to illustrate and exemplify this invention, one embodiment thereof will be described in connection with the accompanying drawing, but it is to be understood that my invention is not necessarily limited thereto and that this embodiment is presented principally by way of illustration and exemplification of this invention and not limitation. In the drawing Fig. 1 shows a tank constructed in accordance with this invention; and Fig. 2 shows the layers of the wall structure in detail.

A tank is shown generally at 1 and the wall thereof at 2. Referring more particularly to Fig. 2, the outer layer of the wall is shown at 3 and this may comprise a tough wear-resistant material such as a rubber impregnated rayon, for example. Layers 4 and 6 comprise a material which swells and expands when contacted by the contents of the container to effect a sealing of a hole left as by a projectile, and for such hydrocarbons as gasoline, benzene and lubricating oils, for example, especially gasoline, a material such as latex is satisfactory. At 5 is a layer of such a material as vulcanized rubber which adds elasticity to the wall structure as a whole, and appears to cushion the shock of a high speed projectile. The inner lining is shown at 7 and comprises a polyvinyl acetal resin in accordance with this invention.

It is to be understood that other outer layers of wall structure may be used in combination with the novel inner liner of this invention, but that for a self-sealing container it is highly desirable that such outer layers include an element effective to seal a hole made by a projectile and

that the outer layers be such that the wall structure as a whole is sufficiently strong, elastic and non-tearing that a projectile passing there-through leaves a hole having a sufficiently small opening that the sealing means can function properly.

The inner liner 1 comprising the polyvinyl acetal is preferably in the form of a relatively thin sheet of such a resinous material. It may, however, with some advantage comprise a coating of such a resin applied to the inner surface of the outer layers, and, moreover, may be made by coating or impregnating such a supporting material as duck, plywood or veneer, or by laminating a thin film of the resin to such a supporting material. As pointed out above, however, a thin sheet of the resinous material is preferred, since this makes it possible to obtain greater advantages from this material in accordance with this invention.

The polyvinyl acetals for use in accordance with this invention may be made by the polymerization of vinyl acetate or other vinyl esters, followed by saponification and reaction with an aldehyde. These esters may be polymerized to various degrees and under different conditions before hydrolysis and reaction with the aldehyde. Moreover, the resulting acetals may contain different proportions of ester, hydroxyl and acetal groups corresponding to the degree of hydrolysis and acetalization of the polymerized ester. It is desirable to select those polyvinyl acetal resins which are least affected or substantially unaffected by the contents of the container; for example, for a gasoline tank, it is desirable to use those polyvinyl acetal resins which are gasoline insoluble or the least affected by gasoline.

Polyvinyl formaldehyde acetals, such as disclosed in the patents referred to above, for example, are especially suitable. Usually the polyvinyl formals will be made by polymerizing the vinyl ester to such a degree that a one-molar solution of the polymer in benzene has a viscosity of from about 10 to 100 centipoises at 20° C., hydrolyzing and reacting such polymer with formaldehyde to produce a polyvinyl formal resin having from substantially none to about 33 per cent acetate calculated as polyvinyl acetate and from about 5 to about 15 per cent hydroxyl calculated as polyvinyl alcohol, by weight, and the rest substantially acetal. In general it is desirable to use a resin having a hydroxyl content greater than about 5 per cent and an acetate content less than about 15 per cent. Thus, such a polyvinyl formal resulting from the polymerization of vinyl acetate and hydrolysis and reaction of the polyvinyl acetate with formaldehyde to form a polyvinyl formaldehyde acetal resin containing substantially 4 to 10% hydroxyl groups calculated as polyvinyl alcohol, 9.5 to 13% acetate by weight, calculated as polyvinyl acetate, and the rest substantially acetal, is an example of a polyvinyl acetal suitable for the present invention.

For a high resistance to hydrocarbons, such as gasoline and benzene, it is preferred to use a polyvinyl formal resin in general that has a relatively low acetate content, preferably below about 10%, a relatively high hydroxyl content, preferably above about 10%, but not so high as to render the material subject to deterioration by water have been found especially desirable because of the high resistance to such hydrocarbons as gasoline or benzene, such as, for example, a polyvinyl formal having 14.6% hydroxyl calculated as polyvinyl alcohol and 1.5% acetate, and a poly-

vinyl formal having a 13.4% hydroxyl content and a 8.7% acetate content.

As another example, a polyvinyl acetal suitable for this invention results from the polymerization of vinyl acetate to such a degree that a one-molar solution of the polymer in benzene had a viscosity of substantially 60 centipoises at 20° C., and the hydrolysis and reaction of the polyvinyl acetate with butyraldehyde to form a polyvinyl acetal resin containing substantially 17 to 21 per cent hydroxyl groups calculated as polyvinyl alcohol, 3% or less acetate by weight and the rest acetal.

Moreover, this invention comprehends the use of other aldehydes, such as acetaldehyde, or mixtures thereof, or even ketones in making suitable polyvinyl acetals to be used in accordance with this invention. Thus, for example, acetaldehyde, propionaldehyde, valeraldehyde, and hexaldehyde may be used. In general it is desirable to use a resin which will not be deteriorated to any substantial extent by the contents of the container, and in the case of such a hydrocarbon as gasoline or benzene, an acetal made with such lower aldehydes as formaldehyde or butyraldehyde is preferred.

The film or sheet of polyvinyl acetal for this invention may be made by any of the known methods of forming such a resin into a film or sheet, which should, of course, be non-porous for a fluid container. The resin may be extruded by means of suitable apparatus to produce a sheet, or a solution of the resin in a suitable solvent may be cast in any well-known manner and a film or sheet formed by evaporation of the solvent. Sheets of any desired thickness may be formed by these methods and a thickness of about .025 inch is usually suitable.

It is a significant feature of this invention that when the polyvinyl acetal resins as described above are modified with certain plasticizers as described below striking new and unexpected results are obtained. In order to illustrate this feature of the invention the following example is given: a polyvinyl formal resin resulting from the polymerization of vinyl acetate to such a degree that a one-molar solution in benzene has a viscosity of about 15 centipoises at 20° C. and the hydrolysis and reaction of the polyvinyl acetate with formaldehyde to form a polyvinyl acetal resin containing substantially 6-8 per cent hydroxyl groups calculated as polyvinyl alcohol, 11-13 per cent acetate calculated as polyvinyl acetate, and the rest substantially acetal, was plasticized with diacetin in proportion of 80 parts of diacetin by weight to each 100 parts of the resinous material. The resin thus plasticized was formed into a sheet about .040 inch thick.

Sheets of the material described above were tested for flexibility at low temperatures. Sheets at a temperature of -40° F. were bent abruptly, but did not crack or break and showed a satisfactory flexibility at this very low temperature. Other sheets after immersion in a mixture of 38% benzene and 62% of 100 octane aviation gasoline at 120° F. were also bent at -40° F. Some decrease in flexibility was found, but the material was still highly satisfactory considering the extreme test applied.

A test for extraction of the plasticizer was carried out by immersing and agitating 1 x 1/2" pieces of a plastic sheet .025" thick in a mixture of 60% by volume A. S. T. M. naphtha and 40% benzene for 48 hours at room temperature. Although the weight loss of plasticizer was about

11%, the flexibility remained highly satisfactory. Curves of extraction of plasticizer against time reach a limiting value of around 16 per cent in about one month.

Another extraction test simulating but accelerating conditions of actual service of a gasoline tank was made by filling small bags made of the plastic material with gasoline and placing them in a sealed can at an elevated temperature of 120° F. The gasoline in the bags was stirred occasionally. After six weeks no significant deterioration of the bags was observed. The bags showed only a very slight stiffening and were quite flexible even at low temperatures. At the extreme low temperature of -36° C. these bags could still be crushed in the hand and, although somewhat stiff at this very low temperature, did not break or shatter. A similar test using a mixture of 60% by volume 100 octane aviation gasoline and 40% benzene, showed only a slight increase of stiffening effect on the plastic material. In general, extraction rates with A. S. T. M. naphtha with or without benzene drop off rapidly with time and are somewhat higher at higher temperatures. However, it is significant that the plasticizer extracted is not harmful to motor fuel, such as aviation gasoline, and not harmful to the motor in which such motor fuel is used.

This resin plasticized with diacetin as described above showed, in addition to a high resistance to a motor fuel comprising essentially paraffinic hydrocarbons, such as an aviation gasoline, an unusually high resistance to extraction by aromatic hydrocarbon motor fuels, such as benzene. Hence, this material is exceedingly useful as a liner for tanks intended for motor fuels containing aromatic hydrocarbons, such as benzene. Moreover, this material shows an especially low extraction at low temperatures.

Sheets of this material .040" thick were tested for diffusion with gasoline and with a mixture of 60% by volume aviation gasoline and 40% benzene. The average diffusion in fluid ounces per square foot per day for a period of one week was .017 for the gasoline and .055 for the mixture containing the benzene. In general, where the average for a week was found to be about .02 fluid ounces per square foot per day the average for eleven weeks was found to be about .007. It is found that diffusion is substantially independent of thickness and the rate of diffusion drops off rapidly with time, becoming substantially zero after about one month.

Gasoline tanks made up in accordance with this invention using sheets of this plastic material plasticized as described above were subjected to tests and found highly satisfactory. Two tanks after being filled with gasoline for a considerable period of time were subjected to firing tests with a .50 caliber machine gun at -20° F. These tanks were successful in preventing leaks even though bullets passed through the tanks. Although some small cracks were observed in the plastic material when the tank was opened for inspection, no leaks developed under the extreme conditions of this test.

The plastic material of this invention as described above may be used as a liner for a gasoline tank or other container in the form of sheets cut to proper form which may be seamed with a hot iron, or preferably by wetting laps with an active solvent for the material, such as ethylene dichloride, rolling the lap down, and drying in an oven for about an hour at 140° F. The plastic liner may be affixed to the rest of the

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wall structure by any suitable means, such as by any suitable cement. For example, in affixing this plastic material to such wall material as latex, neoprene, fabric, fiberboard etc., a polyvinyl formal dope containing an adhesive followed by a neoprene type cement has been found satisfactory. It is also contemplated that the liner may be made up as a separate complete unit preformed to fit suitably the inside of a tank and adapted to be inserted therein, and may be inserted into position in the inside of the tank forming therein a flexible inner container for the material such as gasoline placed in the tank.

Although in the specific plasticized composition described above the proportion of plasticizer is 80 parts of diacetin to 100 parts of the polyvinyl formal resin, which is the preferred proportion, desirable results may be obtained with greater or smaller proportions of plasticizer in accordance with this invention. Proportions of plasticizer from about 40 to about 100 parts to each 100 parts of resinous material may be used. Less than about 40 parts of plasticizer may render the material too brittle, and more than 100 parts may render it too soft. Moreover, extraction of plasticizer is greater when larger amounts of plasticizer are used so that little advantage is obtained in using larger amounts in making a gasoline tank liner. It must be emphasized, however, that the most satisfactory results are obtained with about 80 parts of plasticizer as described above.

Although diacetin gives far superior results for the purpose and as described above, it has also been found that triacetin may also be used with satisfactory results. Moreover, still other compounds may be used, and therefore, this invention comprehends the use of esters of polyhydric alcohols with aliphatic acids, particularly fatty acids, including especially esters of glycerol and polyethylene glycols with such acids, which esters have more than five and less than twelve carbon atoms. Examples of such compounds are diacetin, triacetin, dipropionin, dibutyryne, diethylene glycol acetopropionate, diethylene glycol dipropionate, diethylene glycol diacetate, diglycerol acetate, and triethylene glycol diacetate.

I claim:

1. A self-sealing gasoline container comprising a self-sealing means and an inner liner comprising a polyvinyl acetal resin made with formaldehyde plasticized with diacetin.

2. A self-sealing gasoline container as defined in claim 1 in which the diacetin is present in the proportion of from about 40 to about 100 parts by weight of diacetin to each 100 parts of resin.

3. A self-sealing gasoline container as defined in claim 1 in which the diacetin is present in the proportion of about 80 parts by weight of diacetin to each 100 parts of resin.

4. An inner liner for a hydrocarbon motor fuel container comprising a preformed container

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adapted to be inserted in a tank structure and made with a polyvinyl formal resin containing a plasticizer comprising diacetin.

5. A self-sealing container comprising an inner liner made with a polyvinyl formal resin containing a plasticizer comprising diacetin, and a self-sealing means on the outside of the liner.

6. A self-sealing gasoline container as defined in claim 1 in which the polyvinyl formal resin is substantially identical with the resin which results from polymerization of vinyl acetate to form polyvinyl acetate and the hydrolysis and reaction of the polyvinyl acetate with formaldehyde to form a polyvinyl acetal resin containing more than about 5% hydroxyl groups calculated as polyvinyl alcohol and not more than about 15% acetate calculated as polyvinyl acetate, and the rest substantially acetal.

7. A self-sealing container as defined in claim 1 in which the polyvinyl formal resin is substantially identical with the resin which results from polymerization of vinyl acetate to form polyvinyl acetate and the hydrolysis and reaction of the polyvinyl acetate with formaldehyde to form a polyvinyl acetal resin containing more than about 10% hydroxyl groups calculated as polyvinyl alcohol and not more than about 10% acetate calculated as polyvinyl acetate, and the rest substantially acetal.

8. A self-sealing container for motor fuels and the like, such as gasoline, which comprises a wall having a layer of rubber-impregnated rayon, a layer of latex, a layer of vulcanized rubber, another layer of latex, and a sheet of polyvinyl formal resin as an inner liner, said resin being plasticized with diacetin.

9. A self-sealing wall structure for retaining fluids comprising a self-sealing means and an inner liner comprising a polyvinyl formal resin containing a plasticizer comprising diacetin.

10. A container as defined in claim 4 in which the ester is diacetin in the proportion of about 80 parts to each 100 parts of polyvinyl formal resin.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,053,112	Schnabel	Sept. 1, 1936
2,160,371	Schnabel	May 30, 1939
2,070,331	Darby	Feb. 9, 1937
2,160,372	Stark	May 30, 1939
2,184,443	Smith	Dec. 26, 1939
1,297,305	Thacher	Mar. 11, 1919
2,205,420	Kyrides	June 25, 1940

FOREIGN PATENTS

Number	Country	Date
301,089	Great Britain	Sept. 26, 1929