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3,229,014

METHODS OF MAKING A FLEXIBLE CONTAINER

Original Filed May 31, 1962

3 Sheets-Sheet 1

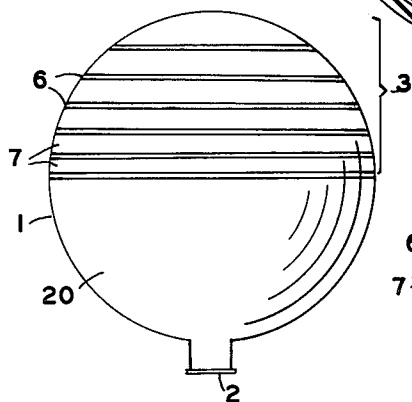
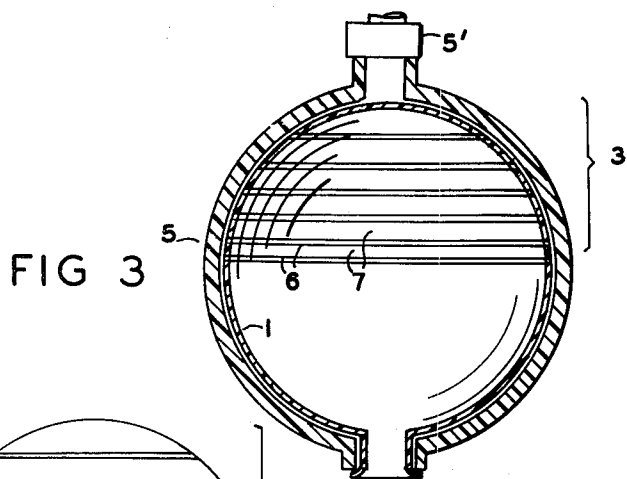


FIG 1

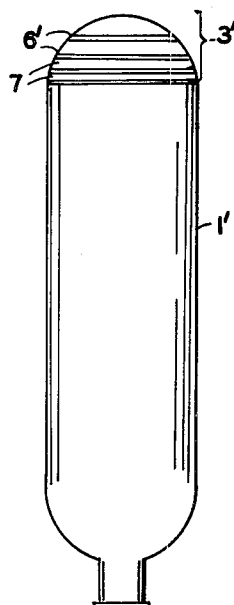


FIG 2

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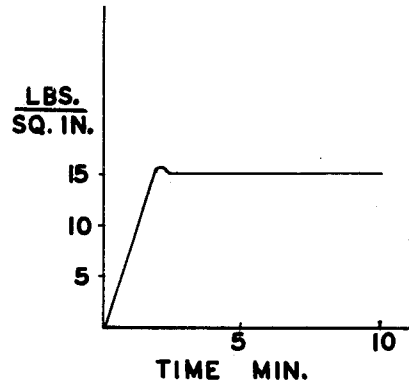
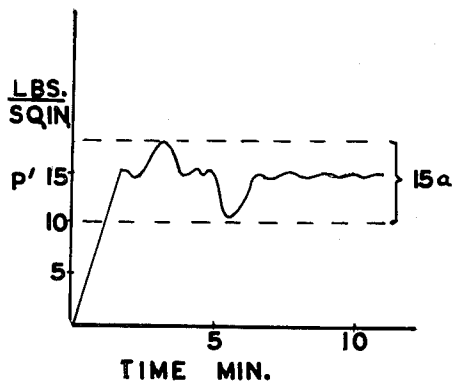
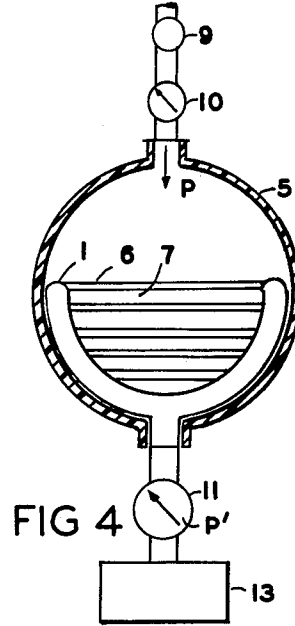
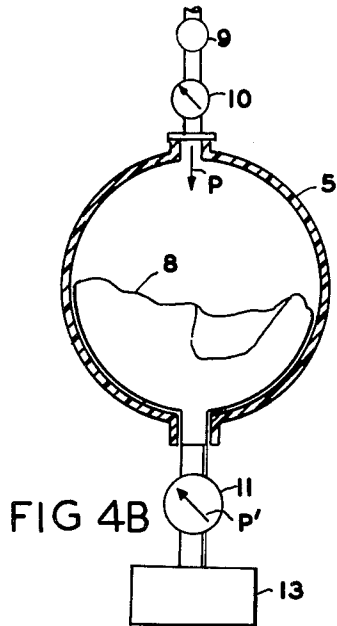
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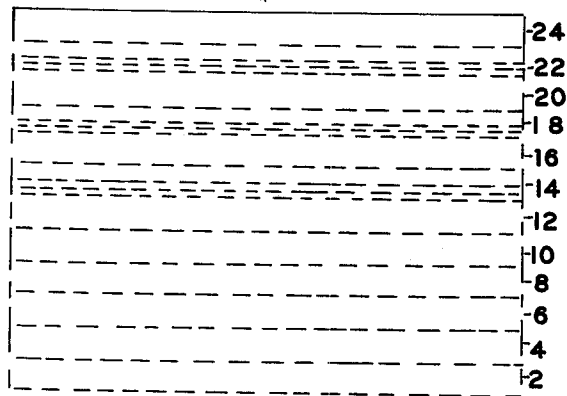
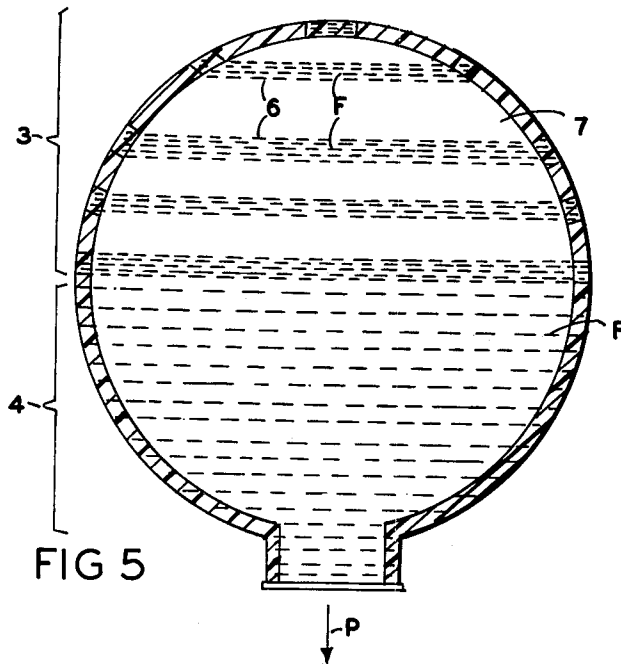
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METHODS OF MAKING A FLEXIBLE CONTAINER

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3 Sheets-Sheet 3



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3,229,014

METHODS OF MAKING A FLEXIBLE CONTAINER

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Original application May 31, 1962, Ser. No. 198,954, now

Patent No. 3,213,913, dated Oct. 26, 1965. Divided

and this application Jan. 28, 1965, Ser. No. 428,823

6 Claims. (Cl. 264-250)

This application is a division of my copending application, Serial No. 198,954 filed May 31, 1962, now Patent No. 3,213,913, and entitled Flexible Containers.

This invention relates to methods of making novel and simple flexible containers for handling reactive liquids.

It is a primary object of this invention to provide methods of making a flexible chemically-inert container designed for storing, transferring, and metering reactive propellants and fuels used in positive propulsion systems. A further object of this invention is to provide methods of making a container constructed in such a manner that the transfer, dispensing, and otherwise releasing of the reactive propulsion fuel is accomplished with improved reliability. A still further object is to provide methods of making a flexible, pressure-dispensing container having unique construction characteristics that will assure steady, stable emergence or dispensing of the contents on demand.

A fuel container of the type with which this invention is concerned is generally termed a "bladder" in the field of rocket or missile propulsion. The bladder is used to positively expel a stored liquid or propellant. The flexible container or bladder is usually designed to fit the inside of a rigid tank with provisions to mount and seal the flexible container or bladder within the tank so that a fuel or propellant may be contained either within a fully expanded bladder or outside of a deflated bladder. Positive expulsion is then achieved by introducing, under pressure, an expellant gas on that side of the bladder opposite the fuel or propellant thereby causing a deflection of the bladder and forcing the fuel or propellant out of the system through a properly arranged discharge line.

Since the bladder is fully collapsing it is susceptible to random wrinkling and folding over most of the surface. Such wrinkling and folding usually results in sharp creases, weak areas, pinholes and eventual failing of the bladder in the expelling operation.

The flexible container or bladder of the type with which this invention is concerned has the unique feature of dispensing various gases, liquids, fuels, propellants under an expellant gas pressure with a pre-arranged pre-devised pattern and array of fold lines, channels and troughs which precludes the random wrinkling patterns and significantly prolongs the usefulness of the container.

A singular feature of the product container of this invention is the rather surprising observation that, the flexible liner as it is made to collapse according to these pre-arranged fold lines, attains a fixed or stabilized volume that does not collapse or otherwise distort to cause irregular dispensing rates, as will be described hereinafter. Another feature is the observation that the flexible plastic container having pre-arranged fold lines retains its collapsing pattern even on intense and random positioning including erratic cycling and attitudes.

The product container of this invention is particularly advantageous in storing, handling, metering and otherwise dispensing a wide variety of gases, fluids and solid slurries that are highly corrosive and cannot be handled in conventional rigid containers. The flexible container described in this invention is constructed of a variety of

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flexible polymeric or plastic materials selected on the basis of ability to withstand chemical attack or dissolution. These plastic materials include high molecular weight resins made from polyethylene, polypropylene, natural and synthetic rubber, and other unique polymers such as polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, and copolymers of tetrafluoroethylene and hexafluoropropylene, vinylidene fluoride and hexafluoropropylene, and such modifications as induced by known methods of cross-linking and grafting with other polymeric components. Any other plastic materials are included which are characterized as having two important attributes: flexibility and chemical inertness to the contained fluid.

These flexible containers are useful and valuable in storing compartmented fluids, for instance, as tank liners, dam storage, positive metering or propulsion systems, and the like, and are provided with simple pressuring means that collapses the flexible container away from an outer casing which is made of rigid, non-flexing material. The containers are also useful in storing and metering on command liquid propellant fuels in missile and spacecrafts. Finally, they are useful in metering reactive chemicals in many industrial processes.

It is therefore an object of this invention to provide methods of making an improved and novel flexible chemical container which through controlled and precise collapsing is used to carry out efficient mixing, diverse chemical reactions, and positive metering of fluids. Other objects and advantages of this invention are made apparent in the following description by reference to the accompanying drawings.

FIGURE 1 is a side view of an embodiment of the invention.

FIGURE 2 is a side view of another embodiment of the invention.

FIGURE 3 is a sectional assembly view of the embodiment of FIGURE 1.

FIGURES 4 and 4B are sectional diagrammatic views illustrating the operation of the invention.

FIGURES 4A and 4C are graphs representing pressure relations for the embodiments of FIGURES 4 and 4B.

FIGURE 5 is a sectional view of the embodiment of FIGURE 1.

FIGURE 6 is a diagrammatic view of the multi-layer construction.

FIGURE 1 is a perspective view of a typical modular design of general type flexible inner containers 1 made principally in the form of a sphere provided with an emergent outlet 2.

It generally comprises a lower portion 20 which is of rigid construction and an upper portion having alternate reinforced strips 6 and non-reinforced strips 7. The container is formed by spraying onto a form many layers of resin material as will be described. The reinforced layers are sprayed on with reinforced material incorporated with suitable masking as will be described hereafter. The form is later dissolved out.

Referring to FIGURE 3, the inner container 1 is mounted inside a rigid outer container 5 which has a valve 5' for introducing a pressure between the inner and outer containers for the purpose of collapsing the inner container and expelling its contents, with a predetermined flow.

FIGURE 2 is a similar perspective view of an inner container 1' made in the form of cylinder with hemispherical geometry at each end of the cylinder.

Referring specifically to FIGURES 1 and 2, the upper hemispherical sections 3 and 3' are provided with polymer modified latitudinal reinforced bands 6 and 6' that direct the pattern of collapse under interstitial pressure, that is

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pressure applied pneumatically or hydrodynamically between outer portion of the flexible inner container 1 and the inner portion of a rigid outer container or shell 5 as shown FIGURE 3.

The latitudinal bands 6 and interposed alternately with unmodified latitudinal bands 7 which comprise the basic polymeric component of the flexible containers such as shown in FIGURES 1 and 2.

In the flexible container produced by the methods of this invention, the alternating latitudinal bands are constructed with distinct differences in flexural stiffness and modulus. It has been discovered that with a difference of as low as 25 percent in flexural or tensile modulus as measured by appropriate procedures, a highly effective and uniform collapse pattern takes place with attendant advantages in volume stability and metering as well as improved container life performance.

FIGURE 4 illustrates the collapse pattern of the latitudinally banded spherical flexible container 1 made from 0.012-inch thick polytetrafluoroethylene as described in ensuing Example I and installed in a "Lucite" acrylic shell 5 so as to enable one to compare visually the physical arrangement with that of an unmodified flexible container 8, FIGURE 4B, made of identical dimensions. In this operation, a pressure P of 15 lb./sq. inch per gauge 10 is valved rapidly through valve 9 into the interstitial region between the flexible containers, filled with water, and the transparent "Lucite" shell 5. The interior container collapses and expels its contents through pressure gauge 11 to tank 13.

The unmodified flexible container 8, FIGURE 4B assumes a highly random, squashed form whereas the modular banded container 1, FIGURE 4, assumes a perfectly symmetrical inversion. The term modular as used in this sense is defined as the existence of regular pre-arranged different moduli or other rigidity constants.

Referring to FIGURES 4A and 4C a remarkable feature is that at the emergent side, the output pressure P' profile with respect to time measured on gauge 11 is extremely erratic or irregular as shown in graph FIGURE 4C for the non-modular normal type of flexible container, whereas that of the container latitudinally modified FIGURE 4B as detailed herein is extremely regular and precise. The irregularity is indicated at 15a FIGURE 4C as the range of variability of about 9 to 17 lbs./sq. inch gauge for with the regular type of container compared to smooth flat pressure of less than 1 lb./sq. in. gauge pressure for the modulated container. This will also be evident in the marked difference in flow rate during the expulsion of liquid contents to be described in ensuing examples.

Inspection of the containers following a series of twelve such pressure operations revealed marked creases and cracks in the non-modulated container during the expulsion of ice-cold water (0°) compared to complete absence of any such effects in the hemispherically modulated container. More detailed features are described as follows:

Example I

A 24 inch diameter spherical flexible container, FIGURE 5, suitable for storage and pressure-expulsion of concentrated fuming nitric acid is constructed of sintered 0.012 inch polytetrafluoroethylene, applied over a replicating aluminum form, which is later dissolved out, corresponding to FIGURE 1 by a series of spray-coatings using a commercial aqueous dispersion of the polymer identified as "Teflon" tetrafluoroethylene fluorocarbon resin, grade 30, sold commercially by E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware. The spray coatings are alternately interspersed with admixture of fine aluminum flake F averaging 2-10 microns in diameter at a thickness of 0.5 micron, and a co-dispersion volume loading, ingredient bases, of 25 volume percent

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of aluminum flake to 75 volume percent of dry, sintered resin indicated by the broken lines in FIGURE 5.

The layers were masked to provide two distinct hemispherical characteristics:

(a) Lower, rigid emergent hemispherical section 4 with a relatively high modulus of 145,000 lb./sq. in., as measured by ASTM procedure D1530-58T, attained by admixture of the aluminum flake, and

(b) Upper, modular-rigid pressure folding hemispherical section 3 comprising alternate latitudinal bands approximately 1 inch $\pm$ $\frac{1}{16}$ in width. The most flexible, non-filled bands 7 comprise basic sintered resin made to a modulus of 70,000 lb./sq. inch. The rigid latitudinal bands 6 are reinforced and have a modulus of 145,000 lb./sq. inch.

For the lower rigid hemispherical portion 4 and latitudinal stiffening bands 6, a cross sectional buildup 16 of the total 0.012-inch was made according to the description shown in FIGURE 6 comprising 24 layers in the following sequence.

Layer:	Composition
24 (external) -----	Resin.
22 -----	Resin+aluminum flake.
20 -----	Resin.
18 -----	Resin+aluminum flake.
16 -----	Resin.
14 -----	Resin+aluminum flake.
12 -----	Resin.
10 -----	Do.
8 -----	Do.
6 -----	Do.
4 -----	Do.
2 (internal) -----	Do.

wherein the internal layers 2-12 are predominantly made of the resin, while the external layers 14-24 are made of resin and aluminum flake to impart the desired higher modulus. For flexible portions all layers are of resin.

Each layer is sintered at 340°-400° C. for 10-30 minutes thereby fusing it to the preceding layer. Each layer is cooled to room temperature before applying the next layer. This sintering process is described in my Patent No. 2,852,811 granted September 23, 1958. Thus as the interstitial pressure P is imposed, the regions 6, FIGURE 5, will oppose the pressure while regions 7 will, with its lower effective modulus, undergo flexure.

Under a liquid propulsion operation comprising concentrated nitric acid made to emerge through a nominal $\frac{1}{32}$ inch stainless steel nozzle under a pressure difference of 15 lb./sq. inch gauge, the following volumetric sequence was measured as compared to an identical design of a container made without the latitudinal, high modular bands.

Expulsion Flow

[Volumetric expulsion pressure: 15 lb./sq. in. gauge]

Time (min.)	Modulated Container (cubic centimeters)		Regular container (control) (cubic centimeters)	
	Accumulated	Incremental	Accumulated	Incremental
0.25 -----	86	86	62	62
0.50 -----	146	60	110	48
0.75 -----	186	40	156	46
1.0 -----	226	40	188	32
1.25 -----	226	40	228	40
1.50 -----	306	40	280	52
1.70 -----	346	40	318	38
2.00 -----	386	40	368	50

The unique feature is the regular dispensing obtained from the modulated container, especially after the first 0.5 minute, in increments of 40 cc. in contrast to the variable expulsion; a feature that cannot be tolerated in situations where accurate time metering is necessary.

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EXAMPLE II

A 12 inch diameter, 0.012 inch thick cylindrical container of the general design shown in FIGURE 2 was constructed with 6 inch radial hemispherical ends, one of which was closed while the other was provided with an emergent opening. The lower, emergent hemisphere and the main cylindrical portion were constructed of a 24 layer coating of polytetrafluoroethylene with 25 volume percent nickel flake interspersed at layers 14, 18, and 20 listed in Example I. The nickel comprised particles with an average flat diameter of 100 microns with an average thickness of 10 microns made by the Metals Disintegrating Company, and identified commercially as their product code MD-750 nickel flake leafing grade.

The upper hemispherical section comprised a series of 9 latitudinal bands approximately 1 inch in width alternating between the nickel resin interlayer and plain resin layer.

The expulsion characteristics of this container filled initially with unsymmetrical dimethylhydrazine under a pressure head of 15 lb./sq. in. gauge are shown in the following tabulation compared with a non-modular expulsion container of equivalent thickness.

Table.—Expulsion Performance

[Pressure: 15 lb./sq. in. Temperature 27.5° C.]

Time (min.)	Modulated Container Volume (cc.)		Non-modulated Volume (cc.)	
	Accumulated	Incremental	Accumulated	Incremental
0.25	78	78	62	62
0.50	120	42	90	38
0.75	160	40	122	32
1.00	200	40	180	58
1.00 to 96.0 minutes pause.				
96.25	240	40	230	70
96.50	280	40	282	52
96.75	320	40	340	38
97.00	360	40	388	48

These results are typical of the difference observed with modulated and non-modulated containers. The modulated container remains substantially the same in providing the time-metered expulsion increment whereas the non-modulated shows serious, erratic expulsion. Of particular significance is the even or constant expulsion, after a pause of 96 minutes in the case of the modulated container in contrast to the extremely variable increment in the case of the non-modulated container. It cannot be over emphasized that the dependable, constant metering in the case of the modulated container is highly important in spacecraft flight where impulses to change or adjust the orbital direction are pre-arranged based on metered reactants serving to provide the necessary propulsion. The performance of the non-modulated container, which undergoes random or crenulated collapse, would be most disastrous if the spacecraft propulsion systems were dependent upon the erratic expulsion.

The above examples merely illustrate the performance characteristics are not intended to be restrictive to the rather obvious modifications and equivalents.

For chemically reactive and corrosive fluids, including gases and mobile slurries, the preferred resins for attaining flexible containers are those derived from fluorinate polymers and elastomers, the latter term applying to a class of rubber-like materials having a higher order of yield and recovery than ordinary resins or polymers. For example, fluorinated polymers are referred to those having a recoverable yield strain of 10 to 30 percent whereas the elastomers as intended in this invention have a recoverable yield strain of 100 to 300 percent. The most preferred fluorocarbon polymers include polytetrafluoroethylene and the related copolymer with hexafluoropropylene produced by E. I. du Pont de Nemours

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and Co., Inc. as "Teflon" 100 FEP series of polymers. These are applied either as single polymer dispersions or as mixed or co-dispersions in ranges from 1 to 99 or 99 to 1 percent, of the respective polymer and copolymer. Flexible containers made of elastomer fluorocarbon such as the copolymer of vinylidene fluoride and hexafluoropropylene, made by E. I. du Pont de Nemours under the trade name "Viton," are also intended in this invention comprising hemispherically modulated construction.

The layered arrangement shown in FIGURE 6, is also modified by various sequences of the metal dispersion interlayers to include any variation including symmetrical or exponential buildup. For instance, high reliability in the expulsion performance has been attained by rearranging the layers shown in FIGURE 6 to include diagonal and stagger patterns across the latitudinal bands. Additionally, the cross-sectional width has been modified to provide feathered, or humped lay-up of the dispersed metal component.

In addition to aluminum and nickel in flaked form, a variety of metals and metal alloys can be used including silver, lead, iron, platinum, stainless steels, tantalum titanium and gold to provide the increased modulus. These can be not only in flake form but also in microscopic and submicroscopic fibrous, acicular and isometric form. Besides metals themselves, a variety of metal oxides, silicides, and other chemically inert materials with respect to the contained fluid can be used to stiffen the structure.

While the uses have been illustrated with pressured expulsion systems, the flexible containers can be used in submersed metering of reagents including incremental introduction in storage tanks and process reactors.

I claim:

1. The process of making a flexible container having a predetermined collapsing pattern comprising the steps of,

providing a form having first and second portions, said second portion having a hemispherical end, spraying multiple layers of reinforced plastic material on said first portion, curing each layer, spraying multiple layers of plastic material on said second hemispherical portion to produce alternate bands of reinforced and non-reinforced plastic material by masking the alternate adjacent bands not being sprayed, curing each layer, said non-reinforced plastic material being flexible, and dissolving out said form.

2. The process of making a flexible container having a predetermined collapsing pattern comprising the steps of,

providing a dissolvable form having first and second portions, said second portion having a hemispherical end, spraying multiple layers of reinforced plastic material on said first portion, curing each layer, spraying multiple layers of plastic material on said second hemispherical portion to produce alternate bands of reinforced and non-reinforced plastic material by masking the alternate adjacent bands not being sprayed, curing each layer, said non-reinforced plastic material being more flexible than said reinforced plastic material, and dissolving out said form.

3. The process of making a flexible container having a predetermined collapsing pattern comprising the steps of,

providing a form having first and second portions, said second portion having a hemispherical end, spraying multiple layers of reinforced plastic material on said first portion, curing each layer, and spraying multiple layers of plastic material on said

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- second hemispherical portion to produce alternate bands of reinforced and non-reinforced plastic material by masking the alternate adjacent bands not being sprayed, curing each layer, said non-reinforced plastic material being flexible. 5
4. The process of making a flexible container having a predetermined collapsing pattern comprising the steps of, 10
- providing a dissolvable form having first and second portions, said second portion having a hemispherical end, 10
- spraying multiple layers of reinforced plastic material on said first portion, 15
- curing each layer, and 15
- spraying multiple layers of plastic material on said second hemispherical portion to produce alternate bands of reinforced and non-reinforced plastic material, by masking the alternate adjacent bands not being sprayed, curing each layer, 20
- said non-reinforced plastic material being flexible. 20
5. The process of making a flexible container having a predetermined collapsing pattern comprising the steps of, 25
- providing a form having first and second portions, said second portion having a hemispherical end, 25
- spraying multiple layers of reinforced plastic material on said first portion, 30
- curing each layer, 30
- spraying multiple layers of plastic material on said second hemispherical portion to produce alternate bands of reinforced and non-reinforced plastic material, by masking the alternate adjacent bands not being sprayed, said non-reinforced plastic material being flexible, 35
- sintering each layer at 340°-400° C. for 10-30 minutes, 35
- and cooling each layer to room temperature before applying the next layer.
6. The process of making a flexible container having

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- a predetermined collapsing pattern comprising the steps of,
- providing a dissolvable form having first and second portions, said second portion having a hemispherical end,
- spraying multiple layers of reinforced plastic material on said first portion,
- curing each layer,
- spraying multiple layers of plastic material on said second hemispherical portion to produce alternate bands of reinforced and non-reinforced plastic material by masking the alternate adjacent bands not being sprayed, said non-reinforced material being flexible,
- sintering each layer at 340°-400° C. for 10-30 minutes,
- cooling each layer to room temperature before applying the next layer,
- and dissolving out said form.

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