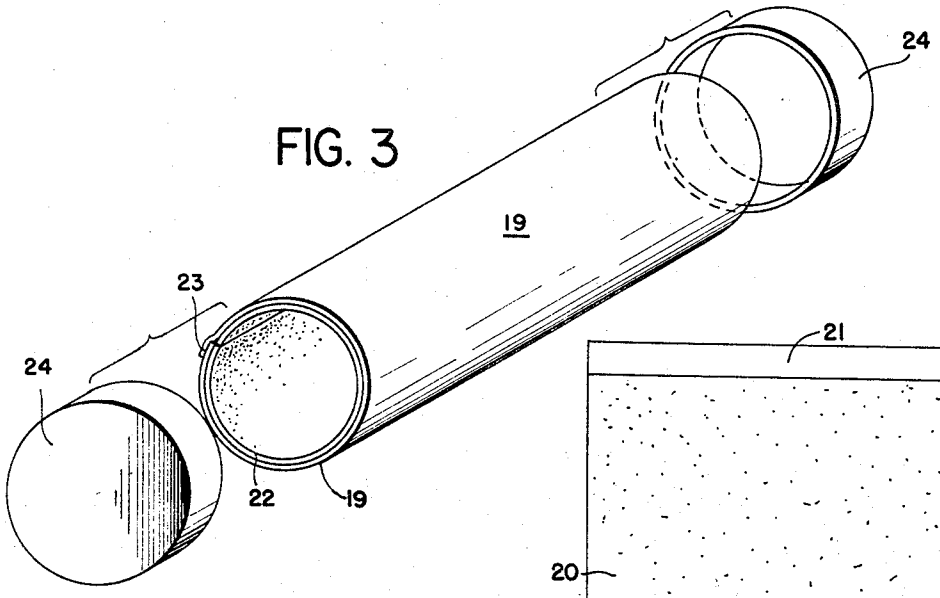
Oct. 22, 1968 A. F. REILLY 3,407,111

RIGIDIZABLE STRUCTURES AND PROCESS

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FIG. 3



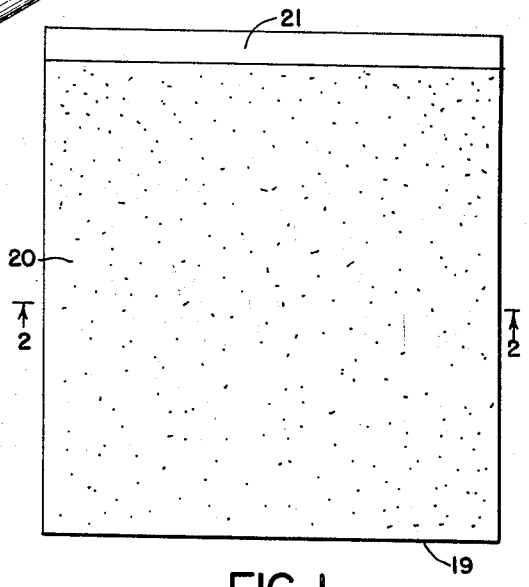
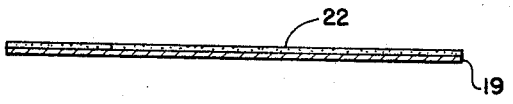


FIG. 1

FIG. 2



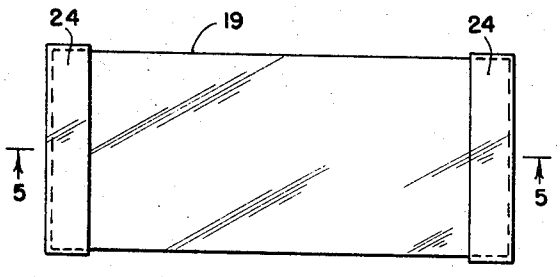
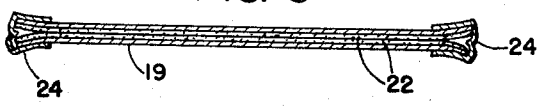


FIG. 4

FIG. 5



INVENTOR.
ALBERT F. REILLY
BY Gene O. Erickson
ATTORNEY

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FIG. 6

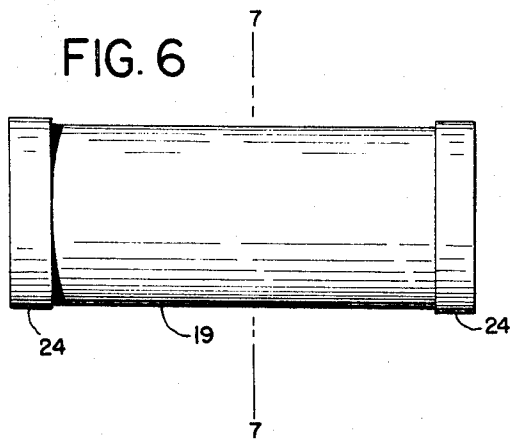
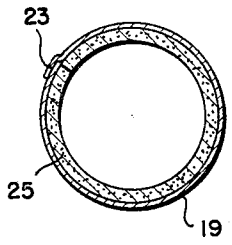


FIG. 7



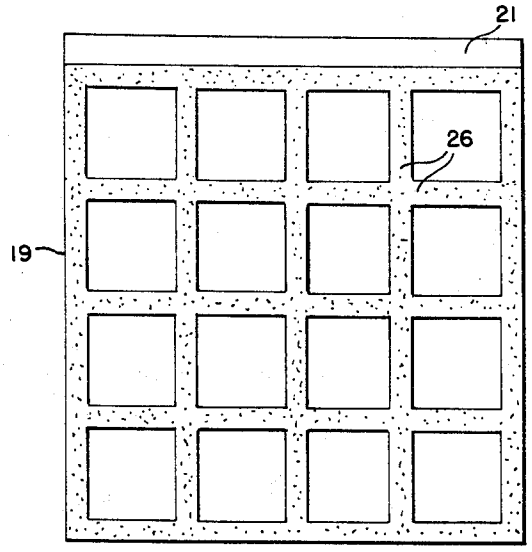


FIG. 8

INVENTOR.
ALBERT F. REILLY

BY Gene O. Enockson

ATTORNEY

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3,407,111

RIGIDIZABLE STRUCTURES AND PROCESS

Albert F. Reilly, Bloomfield Hills, Mich., assignor to General Mills, Inc., a corporation of Delaware

Filed Oct. 29, 1963, Ser. No. 319,796
13 Claims. (Cl. 161—160)

The present invention relates to a process for preparing rigidized structures from pliant foldable material. It also relates to the rigidizable structures used in such process.

Since the advent of space exploration, many types of vehicles or structures have been placed in orbit around the earth. For the most part these vehicles, for example solar collectors, communications satellites and capsules, are small in size due to the present limited boosting power of the rockets used in orbiting said vehicles. In order for larger structures to be orbited, they must be capable of being compressed into a small amount of space and then released and inflated at or sometime after entering the predetermined orbit. Large balloons have been so orbited. However, their usefulness has been limited since their lack of rigidity and strength results in early destruction thereof. It would be highly desirable to provide structures or vehicles which could be folded or compressed into a small space and which could be released, expanded and rigidized upon being placed in orbit.

While such rigidizable structures would find particular utility in space exploration, their use would not be limited thereto. Thus they could be used in shelter kits and the like. The conventional canvas tent has gained great importance as a basic piece of equipment in military operations due to its ability to be compactly packaged. However, the conventional canvas tent is not without disadvantages. Thus each tent requires its own set of tent poles, pegs and guy ropes. These add materially to the equipment carried, for example, by paratroops and rangers. It would be highly desirable to provide an expandable structure which could be used as a shelter, which could be compactly packaged, and which would eliminate the need for a portion or all of the extra equipment needed to erect conventional canvas tents. Other uses for such compact, expandable and rigidizable structures will be obvious to those in the art.

It is therefore an object of the present invention to provide novel rigidizable structures.

Another object of the invention is to provide such structures which can be rigidized merely by the application of moderately elevated temperatures.

It is also an object of the present invention to provide a process for preparing rigidized structures from pliant foldable materials.

These and other objects will become apparent from the following detailed description.

It has now been discovered that a rigidized structure can be prepared from a pliant foldable material by first applying to at least a portion of the surface of the pliant foldable material a layer of an expandable composition consisting essentially of a room temperature stable polyurethane prepolymer and then heating the expandable composition to temperatures above about 100° C. to cause same to expand and rigidize the pliant foldable material.

In the drawings:

FIGURE 1 is a plan view of a rectangular piece of pliable foldable material having a substantial area covered by a layer of an expandable composition.

FIGURE 2 is an enlarged sectional view taken along line 2—2 of FIGURE 1.

FIGURE 3 is an exploded perspective view of a foldable tubular structure prepared from the pliable foldable material of FIGURE 1.

FIGURE 4 is a plan view of the sealed tubular structure of FIGURE 3 in a folded or flattened state.

FIGURE 5 is an enlarged sectional view of the folded and sealed tubular structure taken along line 5—5 of FIGURE 4.

FIGURE 6 is a plan view of the rigidized, tubular structure prepared by the application of heat to the sealed structure of FIGURE 4.

FIGURE 7 is a sectional view of the rigidized tubular structure taken along line 7—7 of FIGURE 6.

FIGURE 8 is a plan view of a rectangular piece of pliable foldable material having strips covered by a layer of an expandable composition.

The expandable composition used in the present invention consists essentially of a polyurethane prepolymer having a portion of the free isocyanato groups blocked, preferably with a tertiary alcohol having less than ten carbon atoms. "Polyurethane prepolymers" are well known in the art. This term refers to polymers having a multitude of organic segments connected by means of organic linkages and also containing a large amount of unreacted isocyanato groups. These materials are prepared by reacting a large excess of a diisocyanate with a compound having an active hydrogen such as alcohols, acids, amines, water, etc. The most commonly used active hydrogen compounds are hydroxyl terminated polyester and polyether resins. A wide variety of these materials have been employed in the preparation of polyurethane prepolymers. Preparation of such materials is described in Rubber Chemistry and Technology, vol. XXXIII, p. 1259 (1960). Polyesters and polyethers specifically synthesized for use in polyurethane resins are readily commercially available. These materials are preferably employed in the present invention.

A wide variety of diisocyanates are useful in preparing the polyurethane prepolymers. Specific examples of such diisocyanates include methylene bis(4-phenyl isocyanate), toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate and hexamethylene diisocyanate. These diisocyanates vary somewhat in their reactivity. The preferred diisocyanates are methylene bis(4-phenyl isocyanate), toluene-2,4-diisocyanate and toluene-2,6-diisocyanate. Mixtures of the latter two diisocyanates are particularly preferred.

The polyurethane prepolymer is preferably treated with a tertiary aliphatic alcohol having less than ten carbon atoms. The preferred alcohols are tertiary butyl alcohol and tertiary amyl alcohol. The tertiary alcohol reacts with free isocyanato groups to form a blocked isocyanato group. This reaction is illustrated by the following equation:

$$Y{-}N{=}C{=}O + HOCR_3 \longrightarrow Y{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OCR_3$$

where Y is the remainder of the polyurethane prepolymer molecule and R is a lower aliphatic radical. Upon heating the blocked isocyanato group, a decomposition occurs. It is believed that the decomposition products are a primary amine, carbon dioxide and unsaturated hydrocarbon. For example, if tertiary butyl alcohol is used as the blocking agent, the reaction could be illustrated by the following equation:

$$Y{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OC(CH_3)_3 \longrightarrow YNH_2 + CO_2 + CH_3{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3$$

where Y is as previously defined.

Thus, when the expandable composition is applied to the pliable foldable material and then heated, the blocked isocyanato groups decompose to form a primary amine,

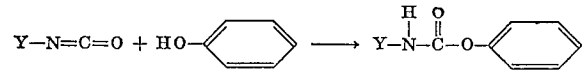
which will react very rapidly with the isocyanato groups to speed the polymerization of the urethane polymer. The carbon dioxide and the olefin provide blowing agents to help form the foam bubbles.

In addition to the polyurethane prepolymer as above described, the expandable composition contains a stable heat-dehydratable compound to aid in the polymerization reaction and in the formation of a suitable quality foam. By "stable" is meant that the hydrogen atoms in the compound will not react with the isocyanato groups at common storage temperatures. A wide variey of organic and inorganic compounds may be used to provide the water. It is preferred to employ a compound which decomposes in approximately the same temperature range as the blocked isocyanate which is used in the composition. Generally, hydrates of organic and inorganic salts are suitable. Boric acid is highly effective for this purpose. This compound decomposes in a very desirable temperature range, and is extremely stable in respect to the blocked isocyanate polymers. Boric acid provides expandable compositions which are stable over a period of several months at ambient room temperatures under substantially moisture-free atmospheres. Whatever compound is employed, it is desirable that the water be freed under reaction conditions at temperatures of about 100–200° C. Preferred temperatures of reaction are 100–160° C.

The polyurethane prepolymer preferably contains from 20 to 35% free isocyanato groups prior to the reaction with the tertiary alcohol. After reaction with the tertiary alcohol, the blocked prepolymer should contain approximately 0 to 20% free isocyanato groups. Since the decomposition of the blocked isocyanato group provides compounds having active hydrogen atoms, a balance can be struck between the amount of blocking agent employed and the amount of dehydratable compound employed. Preferred amounts of the stable heat dehydratable compound based on the total of the expandable composition are 0.5 to 15% by weight.

In many cases, it is desirable to add an additional amount of polyether or polyester resin as a reactant in the blocking reaction. Thus, the reactants in the blocking reaction would be polyester or polyether resin, a polyurethane prepolymer, and a tertiary alcohol. Generally, 10 to 30% by weight, based on the amount of prepolymer, of the resin is preferred.

The blocking reaction can also less preferably be accomplished by treating the polyurethane prepolymer with a phenolic compound. The preferred phenolic compounds are phenol, the alkyl-substituted phenols such as p-nonylphenol and p-dodecyl phenol, cresol, and halogen-substituted phenols such as m-chlorophenol. The phenol reacts with free isocyanato groups to form a blocked isocyanato group. This reaction is illustrated by the following equation:



where Y is the remainder of the polyurethane prepolymer molecule. Upon heating the blocked isocyanato group, the reaction reverses and there is obtained a free isocyanate and a phenolic compound.

Other blocking agents which form heat decomposable adducts with isocyanato groups can be employed. Representative of such compounds are diethyl malonate, ethyl acetoacetate and the like.

Any of the catalysts conventionally used to prepare polyurethanes can be employed to accelerate the curing of the polyurethane prepolymers employed in the present invention. The most preferred agents are the organotin compounds and the tertiary amines. Useful catalysts include bismuth nitrate, lead 2-ethyl-hexoate (25% Pb), lead benzoate, lead oleate, sodium trichlorophenate, sodium propionate, lithium acetate, potassium oleate, tributyltin chloride, dibutyltin dichloride, butyltin trichloride, stannic chloride, tributyltin O-phenylphenate, tributyltin cyanate, stannous octoate, stannous oleate, dibutyltin di(2-ethylhexoate), dibutyltin dilaurate, dibutyltin diisooctylmaleate, dibutyltin sulfide, dibutyltin dibutoxide, dibutyltin bis(acetylacetonate), di(2 - ethylhexyl), tin oxide, titanium tetrachloride, dibutyltitanium dichloride, tetrabutyl titanate, butoxititanium trichloride, ferric chloride, ferric 2-ethylhexoate, ferric acetylacetonate, antimony trichloride, antimony pentachloride, triphenylantimony dichloride, uranyl nitrate, cadmium nitrate, cadmium diethyldithiophosphate, cobalt benzoate, cobalt 2-ethylhexoate, thorium nitrate, triphenylaluminum, trioctylaluminum, aluminum oleate, diphenylmercury, zinc 2-ethylhexoate, zinc naphthenate, nickelocene, nickel naphthenate, 1-methyl - 4 - (dimethylaminoethyl) piperazine, N - ethylethylenediamine, N,N,N',N' - tetramethylethylene-diamine, triethylamine, 2,4,6-tri(dimethylaminomethyl)phenol, N - ethylmorpholine, 2 - methylpyrazine, dimethylaniline, nicotine, molybdenum hexacarbonyl, cerium nitrate, vanadium trichloride, cupric 2-ethylhexoate, cupric acetate, manganese 2-ethylhexoate, triphenyl phosphine, methyldiethanol amine, diethylethanol amine, and tributylamine. It is highly preferred to load catalysts on molecular sieves before incorporation into the expandable composition. This permits the catalyst to remain inert until the expandable composition is heated.

A foam stabilizer can also be used. Typical stabilizers include a group of compounds commonly referred to as silicone surfactants. Generally, these materials are polymers or copolymers of dimethyl siloxane.

Inert fillers can also be included in the expandable compositions. Illustrative of such materials are graphite, Dixie clay, aluminum powder, Celite and the like.

The expandable composition consisting essentially of the polyurethane prepolymer can be applied to the pliable foldable materials in a variety of ways. Thus, the expandable composition can be prepared in situ on the surface of the pliable materials. In this respect, the reactants can be mixed thoroughly under anhydrous conditions and immediately applied to the pliable materials. The composition is thus formed in situ under anhydrous conditions at ambient room temperatures. The expandable composition can first be prepared and then admixed with a suitable solvent, such as dichloromethane. This solution can then be brushed, rolled or the like onto the pliable foldable material and the solvent allowed to evaporate under anhydrous conditions. A preferred method is to prepare the expandable composition, produce a powder from same and apply the powder to the surface of the pliable foldable material which surface has been treated with an adhesive. The powder sticks to the adhesive. The adhesive is selected from those that do not contain large amounts of reactive hydrogen. One such adhesive is a viscous, sticky polyisocyanate which not only serves as the adhesive but also may enter into the ultimate curing reaction upon application of heat.

Structures of various shapes and sizes may be prepared by the process of the present invention. The drawings are illustrative of one preferred embodiment of the present invention. FIGURE 1 is a plan view of a rectangular piece of pliable foldable material **19** which has a substantial area **20** thereof covered by a layer of an expandable composition consisting essentially of the polyurethane prepolymer and an area **21** which has not been coated with the expandable composition. FIGURE 2 is an enlarged sectional view taken along line **2—2** of FIGURE 1 showing the pliable foldable material **19** and the expandable composition **22**.

FIGURE 3 is an exploded perspective view of a foldable tubular structure prepared from the coated pliable foldable material **19** of FIGURE 1 wherein the entire inner surface is covered by the layer of expandable composition **22**. The edges of the rectangular piece of pliable foldable material are joined, such as by gluing, at point **23**. The foldable tubular structure preferably is sealed

with end members **24** which sealing can be effected by the use of glue or heat, for example. FIGURE 4 is a plan view of the tubular structure of FIGURE 3 with the ends being sealed by the members **24** and said structure being in a folded or flattened state. FIGURE 5 is an enlarged sectional view of the folded and sealed tubular structure taken along line **5—5** of FIGURE 4.

FIGURE 6 is a plan view of the rigidized, tubular structure prepared by the application of heat to the sealed and folded tubular structure of FIGURE 4. FIGURE 7 is a sectional view of the rigidized, tubular structure taken along line **7—7** of FIGURE 6 showing the expanded, rigid layer of coating composition **25**.

FIGURE 8 is a plan view of a rectangular piece of pliable foldable material **19** which has strips **26** of the surface thereof covered by a layer of an expandable composition consisting essentially of the polyurethane prepolymer and an area **21** which has not been coated with the expandable composition. A rigidized, tubular structure can be prepared from the coated, pliable foldable material of FIGURE 8 in the same manner as illustrated in FIGURES 1–7.

In addition to cylinders as illustrated in the drawings, cubes, spheres, pyramids and the like may also be prepared. The drawings illustrate application of the expandable composition to the pliable foldable material prior to the preparation or forming of a three-dimensional structure therefrom. However, the three-dimensional structure may be first formed and then the expandable composition applied thereto. The inner surfaces are preferably coated with the expandable composition and the rigidizable structures are also preferably sealed to keep out moisture. Of course, sealing is not necessary and/or the expandable composition can be applied to the exterior of the rigidizable structures providing that the resulting structures are stored under anhydrous conditions at ambient room temperatures.

The pliable foldable material is preferably a thin flexible plastic film. Illustrative of such films are those prepared from polyethylene, polypropylene, "Mylar" (Du Pont's polyester resin prepared from terephthalic acid and ethylene glycol), "Saran" (polyvinylidene chloride film available from the Dow Chemical Company) and the like. The expandable composition can be applied to such materials in various thicknesses. Preferably the coating layers will be under about 20 mils in thickness, and even more preferred, about 1.5–10 mils thick. And the expandable composition will be applied in such a manner as to provide the desired rigid structure upon application of heat. For example, the entire surface can be coated or predetermined strips can be layered with the expandable composition. The inner edges of a cube, for example, could be coated. Upon rigidization, the folded cube would assume its full three-dimensional structure.

Since a rigid structure is to be prepared by the process of the present invention, the ingredients of the expandable composition are selected to provide the desired degree of rigidity when heated and expanded. The prepolymer is preferably prepared from an aromatic diisocyanate such as toluene diisocyanate, the active hydrogen compound is preferably a polyether resin, and the blocking agent is preferably a tertiary aliphatic alcohol.

In order to illustrate certain preferred embodiments of the present invention, the following examples are included. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE I

There were mixed 16.7 parts of a polyether resin which consisted mainly of the condensation product of propylene oxide having a hydroxyl number of approximately 595, 100 parts of a polyurethane prepolymer prepared from the above polyether resin and sufficient toluene diisocyanate (80:20 mixture by weight of the 2,4 and 2,6-isomers) to provide a free isocyanate content of 27% and 12.5 parts of tertiary butyl alcohol. The mixture was maintained at 25° C. (±5° C.) under dry nitrogen atmosphere for over about 48 hours. There was obtained a solid, glassy product having a free isocyanate content of about 10%.

EXAMPLE II

A portion of the blocked polyurethane prepolymer of Example I was ground to a fine powder and passed through a 50 mesh screen. One hundred parts of the powder were then thoroughly mixed with 1.5 parts boric acid, 10 parts of a molecular sieve loaded with dibutyltin dilaurate and five parts of a dimethyl silicone copolymer (Union Carbide Silicone L–520). The resulting expandable powder composition is applied to 1.5 inch wide Mylar tape. About 0.25 gram of the powder is applied per lined inch of tape and the adhesive is a sticky polyisocyanate (Curing Agent RC–805 available from E. I. Du Pont de Nemours & Co.). The coated tape is formed into rigidizable tubes (inner surfaces being coated). The tubes are then heated to 130–150° C. for about 20 minutes in a vacuum oven (5 p.s.i.). There is obtained a rigidized tube having fine strength properties.

EXAMPLE III

The same reactants and amounts thereof as set forth in Example I are admixed with 37.5 parts dichloromethane. The resulting reaction mixture is maintained at 25° C. (±5° C.) under dry nitrogen atmosphere until the free isocyanate content is about 8%. A viscous polymer solution is obtained to which is added 1.5 parts boric acid, 10 parts of a molecular sieve loaded with dibutyltin dilaurate and 5 parts of a dimethyl silicone copolymer (see Example II). This dispersion is applied to a film of Mylar using a roller coater. The dichloromethane is allowed to evaporate under anhydrous conditions and the coated film is formed into a foldable cylinder. The cylinder is then heated to about 130° C. for about 25 minutes to produce a rigid structure. The expandable composition on the inner surface of the cylinder is ten mils thick prior to the curing reaction and ⅛ to 3/16 inch thick after such reaction.

EXAMPLE IV

Rigidizable structures are also prepared by forming the polyurethane prepolymer in situ. The following ingredients are mixed thoroughly under anhydrous conditions:

	Parts
Prepolymer (see Exp. I)	30
Polyether resin (see Exp. I)	6
T-butyl alcohol	4
Boric acid	0.5
Catalyst (see Exp. II)	7.5
Silicone (see Exp. II)	4

Thin coatings (1.5–10 mils) of the mixture are immediately applied to sheets of Mylar. The sheets are then maintained at room temperature under anhydrous conditions for several days. Structures are formed from the coated sheets and heated as in Example II. Rigid, well formed structures are thus obtained.

The procedure of Example II is preferred. As indicated above, the rigidizable structures of the present invention can be used for various purposes. They can be folded compactly and released in orbit around the earth where they will be rigidized by the heat available in space and from the sun's rays.

It is to be understood that the invention is not to be limited to the exact details of operation or the compositions, structures and methods shown and described, as obvious modifications will be apparent to those skilled in the art and the invention is to be limited only by the scope of the appended claims.

Now, therefore, I claim:

1. The process of preparing a hollow, rigidized, three dimensional structure from a pliant foldable material which comprises: (1) applying to at least a portion of the surface of the pliant foldable material a layer of an

expandable composition consisting of a room temperature stable polyurethane prepolymer, said composition being applied and distributed in such a manner as to provide the desired rigidized structure after the coated pliant foldable material has been formed into a shape capable of assuming a three dimensional structure on being rigidized and the composition has been expanded; (2) forming the coated pliant foldable material into a shape capable of assuming a three dimensional structure on being rigidized; and (3) heating the expandable composition to temperatures above about 100° C. to expand same and thus rigidize the pliant foldable material and cause same to assume said hollow, rigidized, three dimensional structure fixed solely by the expansion and rigidization of the expandable composition.

2. The process of claim 1 wherein the polyurethane prepolymer is blocked with a tertiary aliphatic alcohol of less than about 10 carbon atoms and has a free isocyanate content of 0 to 20%.

3. The process of claim 1 wherein the expandable composition also contains a stable heat-dehydratable compound.

4. The process of claim 3 wherein the heat-dehydratable compound is boric acid.

5. The process of claim 1 wherein the expandable composition also contains a curing catalyst and a foam stabilizer.

6. The process of claim 1 wherein the expandable composition is applied in the form of powder and the surface of the pliant foldable material is treated with an adhesive prior to such application.

7. The process of claim 1 wherein the pliant foldable material is a thin flexible plastic film.

8. The process of claim 1 wherein the polyurethane prepolymer is prepared from an aromatic diisocyanate and a hydroxyl terminated polyether, the free isocyanate content of said prepolymer is reduced to 0 to 20% by reaction with a tertiary aliphatic alcohol containing less than about 10 carbon atoms and the expandable composition also contains a stable heat-dehydratable compound, a catalyst and a foam stabilizer.

9. The process of preparing a hollow, rigidized, three dimensional structure from a pliant foldable material which comprises: (1) forming the pliant foldable material into a shape capable of assuming a three dimensional structure on being rigidized; (2) applying to at least a portion of the surface of the pliant foldable material a layer of an expandable composition consisting essentially of a room temperature stable polyurethane prepolymer, said composition being applied and distributed in such a manner to the pliant foldable material as to provide the desired three dimensional rigidized structure when the composition has been expanded; and (3) heating the expandable composition to temperatures above about 100° C. to expand same and thus rigidize the pliant foldable material and cause same to assume

said hollow, rigidized, three dimensional structure fixed solely by the expansion and rigidization of the expandable composition.

10. The process of claim 9 wherein the polyurethane prepolymer is prepared from an aromatic diisocyanate and a hydroxyl terminated polyether, the free isocyanate content of said prepolymer is reduced to 0 to 20% by reaction with a tertiary aliphatic alcohol containing less than about 10 carbon atoms and the expandable composition also contains a stable heat-dehydratable compound, a catalyst and a foam stabilizer.

11. A rigidizable structure consisting of a pliant foldable material having at least a portion of at least one of the surfaces thereof coated with a layer of an expandable composition consisting essentially of a room temperature stable polyurethane prepolymer, said pliant foldable material having been formed into a shape capable of assuming a hollow, three dimensional structure on being rigidized, said expandable composition having been applied and distributed in such a manner to the pliant foldable material as to provide the desired hollow, rigidized, three dimensional structure after the same has been expanded and rigidized, and said rigidizable structure being capable of assuming the desired hollow, rigidized, three dimensional structure fixed solely by the expansion and rigidization of the expandable composition.

12. The structure of claim 11 wherein the expandable composition also contains a stable heat-dehydratable compound and the pliant foldable material is a thin flexible plastic film.

13. The structure of claim 11 wherein the polyurethane prepolymer is prepared from an aromatic diisocyanate and a hydroxy terminated polyether, the free isocyanate content of said prepolymer is reduced to 0 to 20% by reaction with a tertiary aliphatic alcohol containing less than about 10 carbon atoms and the expandable composition also contains 0.5 to 15% by weight boric acid and a catalytic amount of dibutyltin dilaurate in the form of a molecular sieve.

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EARL M. BERGERT, *Primary Examiner.*

CLIFTON B. COSBY, *Assistant Examiner.*