CELLULAR RESINS REINFORCED WITH SILICEOUS MATERIAL

Filed May 10, 1961 2 Sheets-Sheet 1

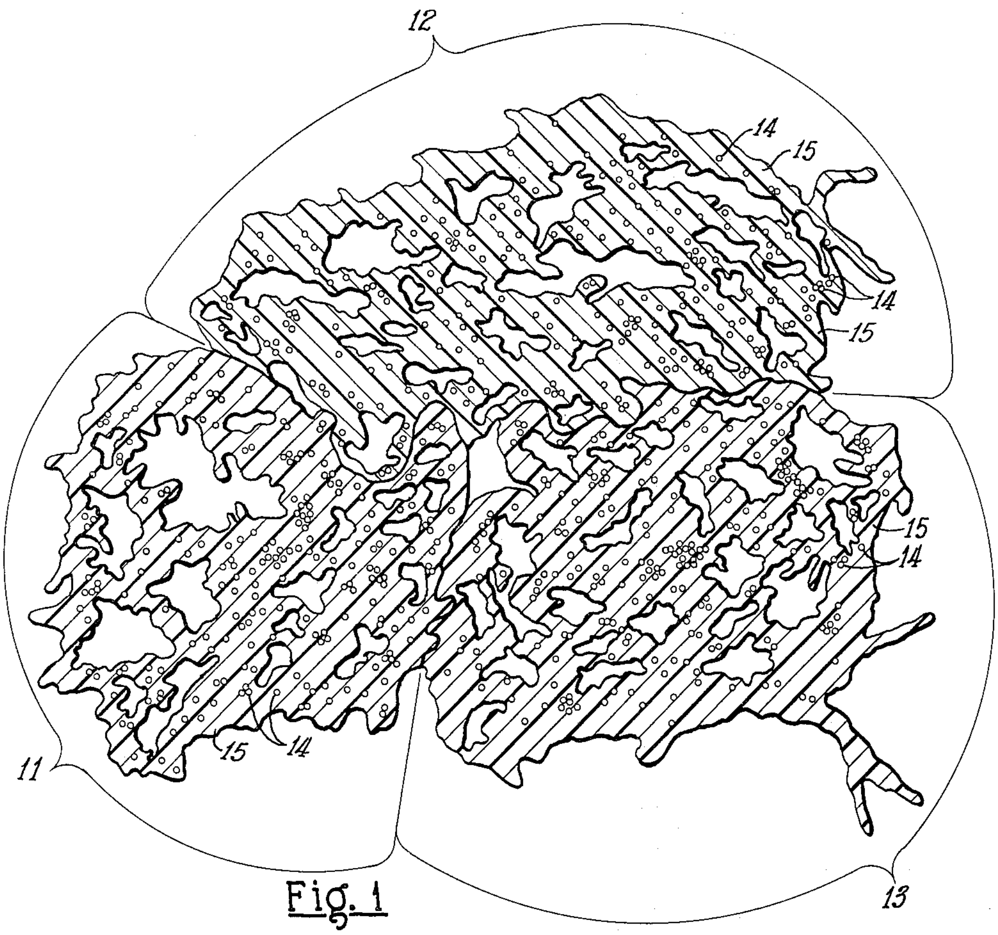

Fig. 1

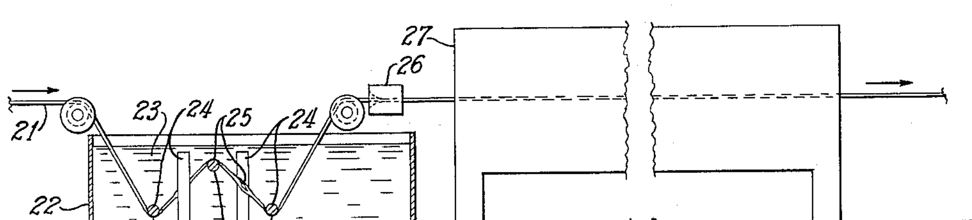

Fig. 2

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April 5, 1966 A. MARZOCCHI ET AL 3,244,545

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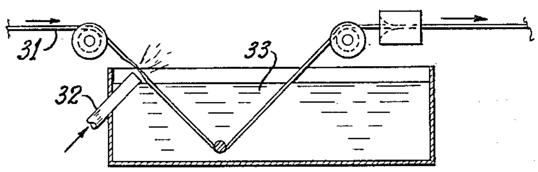

Fig. 3

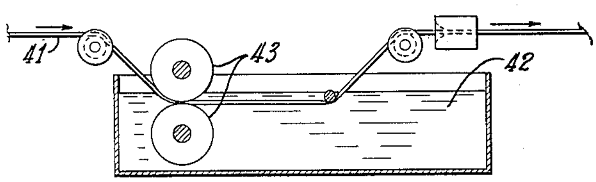

Fig. 4

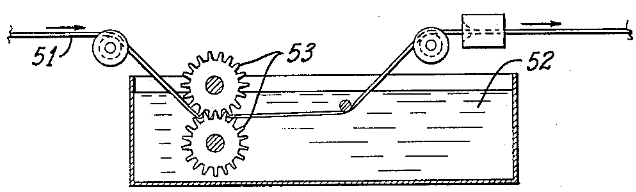

Fig. 5

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CELLULAR RESINS REINFORCED WITH SILICEOUS MATERIAL

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This invention relates to cellular or foamed resins reinforced with siliceous elements and more particularly to cellular resinous matrices which are reinforced by fibrous glass strands.

Due to the inherent characteristics of limited flexibility and extensibility or elongation, poor resistance to compressive, flexural and tensile stresses, and a marked susceptibility to extensive attrition resulting from mutual abrasion, fibrous glass yarns and fabrics have to date been restricted to static or non-dynamic applications such as decorative fenestration fabrics and crude fabrics used in the reinforcement of rigid resinous structures.

These defects, together with a consumer antipathy toward the tactile qualities of such materials, have combined to prevent the utilization of fibrous glass fabrics in such extensive, but dynamic, applications as wearing apparel, upholstery fabrics, carpeting and industrial fabrics. The specified consumer antipathy stems from a preference for the warm and dry tactile qualities evinced by non-synthetic fabrics such as wool and cotton.

In an attempt to upgrade the properties of fibrous glass fabrics, various attempts to coat either the yarn before weaving, or the finished fabric, with a resin or similar material have been undertaken with only limited success. Satisfactory results have been precluded by the fact that such resinous coatings yield a stiff, rigidly bonded yarn or fabric which is prone to the harmful effects of flexing, stretching and mutual abrasion while deterring the elongation or extensibility of the yarns and providing a slick, cold feel which has been found repulsive to the consumer.

In an attempt to overcome these obstacles or impediments, foamed or cellular coatings have also been applied to fibrous glass strands. However, such structures have still failed to yield adequate properties of durability, extensibility and resistance to mutual abrasion. While the presence of the cellular coating may for a time prevent the abrasion of the exterior or circumferential fibers of the strand, the fibers embodied in the core or central portion of the strand are still exposed to this deleterious force. In turn, the damaging affects of flexing upon plural filament structures and compressive or tensile stresses are not prevented since the core of the strand is still of the same nature as that of an uncoated or untreated strand. In addition, the coating fails to impart extensibility to the yarn although its discontinuous surface does serve to enhance the tactile stimuli evoked by bodily contact therewith. The durability of the cellular coating material comprises a further drawback in that such materials, if unreinforced, are highly susceptible to nominal abrasion or wear.

It is an object of the present invention to provide fibrous glass strands which are characterized by unusual qualities of flexibility, extensibility, durability and abrasion resistance, as well as by outstanding tactile properties.

A further object is the provision of elongate, weavable elements comprising cellular, resinous matrices provided with a uniform reinforcement of glass fibers.

Another object is the provision of methods for the fabrication of elongate, weavable elements comprising cellular, resinous matrices provided with a uniform reinforcement of glass fibers.

These and other objects of the invention will hereinafter appear in a more detailed description and for purposes of illustration, but not of limitation, in the accompanying drawing in which:

FIGURE 1 is a sectional view through a yarn processed in accordance with the practice of the invention;

FIGURE 2 is a schematic view of a preferred method and apparatus for the conduct of the invention;

FIGURE 3 is a second embodiment of a method and apparatus for the conduct of the invention;

FIGURE 4 is a third embodiment of a method and apparatus for the conduct of the invention; and

FIGURE 5 is a fourth embodiment of a method and apparatus for the conduct of the invention.

The aforegoing objects are attained by means of the thorough impregnation of fibrous strands with a foamable composition, and the subsequent in situ foaming of the foamable composition.

It has been found that yarn structures exhibiting unusual qualities of durability, elongation and flexibility, and resistance to flexural, compressive and tensile stresses and abrasion, as well as outstanding tactile qualities, may be prepared by means of the deposition, through thorough impregnation and in situ foaming of a cellular resin between and about the individual fibers which are incorporated in the strand or yarn structure. Such a composite structure is depicted by FIGURE 1 wherein a greatly enlarged sectional view through a yarn of the described type is provided. It may be seen that the structure comprises three plied strands designated generally at **11**, **12** and **13** with each strand embodying approximately 200 glass fibers **14**. As is apparent, the plurality of fibers which were originally tightly grouped in a compact strand structure have been dispersed throughout the cellular matrix **15** as a result of the in situ foaming of the resin.

The structures achieved are characterized by ideal properties in that low modulus materials, uniformly reinforced by high modulus elements, are yielded. The low modulus, cellular resin serves to take up compressive forces and consequently protect the fibers from such stresses, while an ideal tensile strength relationship is realized due to the fact that the resin first assumes an applied longitudinal force with such force subsequently being assumed by the high strength fibers prior to the attainment of the breaking point or permanent distortion point of the resin. During the phase when the force is borne by the resin, the fibers are provided with an opportunity to align and consequently mutually assume the total force. In the absence of such a condition, the total force is experienced by individual fibers during the phase of non-alignment, and such fibers are successively broken to provide a tensile strength which is less than that available when all of the fibers are aligned to mutually assume the stress. In addition, the radial compression of the cellular resin upon the application of longitudinal stress, operates to impart elongation or extensibility to the composite structure.

Also desirable is the protection against mutual abrasion which is provided by the presence of the cellular resin between individual filaments and groups of filaments.

Still further, warm, dry, absorbent tactile qualities are yielded by the discontinuous or porous surface of the resin which completely encompasses the yarn or strand.

The thorough impregnation of the strand with the foamable material may be achieved by several methods, although a tortuous path approach involving the utilization of spreader bars is preferred. This method is best demonstrated by FIGURE 2 wherein an uncoated fibrous glass strand **21** is passed into a receptacle **22** and submerged in a bath comprising a foamable material **23**. The strand **21**, while submerged, is conducted through a tortuous path composed of a plurality of staggered spreader bars **24** which are positioned across the width of the receptacle **22** beneath the surface of the foamable material **23** and perpendicular to the path of the strand. Both horizontal and vertical spreader bars **24** may be employed. Since the strand **21** is maintained under constant tension, the roughly cylindrical strand is flattened out as it passes around the spreader bars, as shown at **25**, to the end that the individual filaments embodied within the strand are dispersed or disrupted from their original, dense or tightly picked relationship to thereby permit the penetration of the coating material. The repetition of such dispersion or disruption through the medium of a plurality of spreader bars **24**, insures the complete or thorough penetration of the strand. The strand **21** may then be passed through a die **26** which serves to remove excess coating material from the exterior of the strand, and thence to an oven **27** which serves to activate a blowing agent embodied in the coating material and thereby foam the material.

When large quantities of the coating material are desired, a second application subsequent to the oven treatment may be utilized and may be followed by a second curing or heat treatment. It has been found that as much as 40% by weight of the coating compositions of the examples set forth hereafter may be imparted by the single coating apparatus of FIGURE 2. However a coating comprising 80% or more by weight of the yarn-coating composite may be achieved by merely placing a second coating receptacle and a second oven in line, after the first oven **27**. The two coating materials in the plural coating system may employ different materials and a blowing agent may be employed in one or both of the materials.

While the incorporation of liquid or solid blowing agents in the resin and the subsequent fusion or boiling of these agents to yield void producing gases is the preferred foaming method, other conventional foaming or pore producing methods may be utilized. For example, an inert gas may be incorporated in the resin under pressure, and the mixture then exposed to the atmospheric pressures to expand the gas, or gases generated by an inherent reaction such as the CO_2 yielded by the action of water on polyisocyanates during urethane formation or water vaporized by the exothermic heat of phenolic resin preparations, may be employed to foam the resin.

It should be noted that previous techniques for the coating of fibrous strands with resins, but without provision for the thorough penetration of the strand, have resulted in structures characterized by closely grouped filaments with only the exterior or circumferential filaments possessing a resinous coating. The foaming of the resinous coating of the latter type of structure does not entail the dispersion of the reinforcing elements or fibers throughout the foam and results in a flex and abrasion prone strand which is encased in an unreinforced, low modulus foam.

While the tortuous path or spreader bar technique of FIGURE 2 is preferred, other methods of strand disruption, coupled with a thorough impregnation, may be employed. Two of these methods are illustrated by FIGURES 3 and 4.

FIGURE 3 schematically and sectionally depicts an alternative method for the disruption of the fibrous strand wherein the strand **31** is exposed to the fluid turbulence of a high pressure jet **32** immediately prior to submersion in the foamable coating material **33**. This treatment may be even further enhanced when the fluid disruptive force supplied by the jet **32** is an additional quantity of the foamable material employed as the coating material **33**, rather than a gas.

In still another method, as illustrated by FIGURE 4, the strand **41**, while submerged in the foamable coating material **42**, is passed between the nip of two spaced, opposed rolls **43**, which serve to achieve the lateral displacement of the bunched fibers embodied in the strand and consequently facilitate the thorough impregnation of the strand **14** by the foamable coating material **42**. This effect may also be enhanced through the utilization of rolls **43** having porous or perforate circumferences, and if desired the injection or pressurized feeding of the coating material through such pores or perforations may be adopted.

A further refinement of the apparatus of FIGURE 4 is depicted by FIGURE 5 wherein the strand **51** is submerged in a foamable coating material **52** and passed between the nip of rolls **53** which have fluted surfaces.

It should be noted that immersion techniques have been selected due to the efficiency and ease of penetration of the strand which they provide. However, conventional methods of contact or spray impregnation such as transfer rolls, pads, apron applicators, sprays and jets may also be utilized, when coupled with methods or means which insure the opening of the fibrous bundle and the thorough impregnation thereof with the foamable coating material.

It is not deemed necessary that the impregnation step achieve the opening or disruption and thorough impregnation of each fibrous bundle to the extent that each individual filament is coated, since the disruptive force of the foaming action serves to further the penetration or impregnation. However, the impregnant must penetrate between each major fiber bundle, e.g., the individual strands of a plied yarn, in order to adequately disperse the fibrous reinforcement and preclude the occurrence of massive or predominant groups of bunched fibers.

The fibrous strands employed in the practice of the invention are preferably, although not necessarily comprised of siliceous or glass fibers. This is due to the fact that the properties imparted to the products achieved are greatly enhanced in the case of fibrous glass. However, other fibrous materials such as cellulosic, mineral or synthetic organic fibers may be similarly treated when it is desired to impart a low density bulk or excellent tactile qualities to the strand or yarn, or to avoid the damaging effects of flex, tensile, compressive and abrasive forces. The specific form employed preferably comprises continuous glass filaments grouped into a strand form or a plurality of such strands plied into a yarn structure. The basic strand referred to conventionally comprises approximately 200 grouped glass fibers having diameters of between .0001 and .0007 inch. In addition to strands and plied strands, fibrous glass staple yarns, roving and spun roving provide base materials amenable to the treatments of the invention. The fibrous glass strands utilized may be provided with conventional forming size compositions such as starch, gelatin or resin-based size compositions since the disruptive force of both the coating operation and the subsequent foaming action of the coating material serves to overcome any bonding affect which may be imparted by the forming size composition.

While vinyl polymers and copolymers are the preferred foamable coating materials of the invention, other foamable compositions such as polyurethanes, phenolic, urea-formaldehyde, cellulose acetate, styrene polymers and copolymers, silicone and epoxy resins as well as elastomers such as butadiene and styrene or acrylonitrile copolymers, neoprene and natural rubber may also be utilized. The selection of the solvent system and blowing agent or method in each case, is naturally dependent upon the resin employed and the processing conditions which are preferred or dictated.

A preferred foamable coating material includes the following ingredients which are quantitatively expressed in percentages by weight:

EXAMPLE 1

Polyvinyl chloride	51.4
Dioctyl phthalate	37.7
Epoxy plasticizer	2.7
Barium-cadmium-zinc stabilizer	2.0
Antimony oxide (flame retardant)	2.1
Azodicarbonamide pigment	4.1

Another suitable coating material is set forth in the following example:

EXAMPLE 2

Polyvinyl chloride	53.4
N-didecyl phthalate	16.4
Dioctyl phthalate	19.4
Epoxy plasticizer	5.3
Barium-cadminum-zinc stabilizer	1.7
Antimony oxide	2.4
Azodicarbonamide	1.4

The coating formulations of the invention may be enhanced by and are amenable to the addition of dyes, pigments, plasticizers, emulsifiers, stabilizers and the like. In addition, it has been found that both the tactile qualities and the durability of the foamed materials, are improved by means of the incorporation of short milled fibers in the coating either through the medium of addition to the coating bath or by application and adherence prior to the setting of the coating. While milled cotton fibers are a preferred material, short lengths of glass, cellulosic, mineral or organic fibers are also satisfactory.

In a preferred embodiment, the yarns or strands are coated and the coating is immediately foamed. The yarns may then be woven into a fabric which is satisfactory in such form or the fabric may be subjected to a calendering process which serves to adhere the woven yarns at their points of contact or intersection.

Alternatively, the yarns after coating may be merely dried or cured without foaming, or with only limited foaming, and foaming may be achieved after the yarns are woven into a fabric. This is achieved through a close control of the conditions of temperatures utilized and by the selection of a proper blowing agent or method. When the coating material is foamed after the preparation of the fabric, a relatively impermeable fabric is obtained if the foaming is achieved by passing the fabric through the nip of heated rolls, such as calendering rolls. In this fashion the foam is forced out into the fabric interstices due to the restriction of its lateral movement by the rolls.

One highly desirable product yielded by the invention is a foamable molding compound. This product may be prepared by coating fibrous glass strands with a foamable resin without activating the blowing agent and then chopping the strand into short lengths. The coated strand segments may then be molded into a desired shape and the resinous coating foamed by means of the heat of the molding step or by other conventional means of activation such as chemical reagents. Such molding materials or compounds are preferably composed of chopped strand segments having a length of two inches or less.

It has been found that fabrics prepared in accordance with the invention exhibit unusual utility as upholstering materials, tarpaulin like fabrics, utility or truck covers and the like.

It is apparent that new and useful textile materials exhibiting unusual qualities, and methods for their preparation, have been provided by the present invention.

It is further obvious that various changes, alterations and substitutions may be made in the compositions, methods and products of the present invention without departing from the spirit of the invention as defined by the following claims:

We claim:

1. A method for the preparation of a low density, extensible fibrous glass yarn comprising thoroughly impregnating a bundle comprising a plurality of continuous glass fibers grouped in a substantially parallel relationship with a foamable synthetic resin by opening said bundle to coat each individual fiber, curing said resin, and foaming said resin to laterally displace said fibers individually and disperse said fibers throughout a cellular matrix comprising the foamed product of said synthetic resin.

2. A method as claimed in claim 1 in which said foaming and said curing are achieved concurrently.

3. A method as claimed in claim 1 in which said foamable synthetic resin is polyvinyl chloride.

4. A method as claimed in claim 1 in which said impregnation is achieved by conducting said glass fibers under tension through a tortuous path comprising spaced, staggered guide elements and in contact with said guide elements which serve to divert the course of said fibers and simultaneously to displace the arrangement of said plurality of glass fibers as a product of said tension exerted upon said fibers and said contact of said fibers with said guide elements, and applying said foamable synthetic resin to said fibers while said fibers are displaced.

5. A method as claimed in claim 1 in which said impregnation is achieved by exposing said fibers to fluid turbulence and immediately immersing said fibers in said foamable synthetic resin.

6. A method as claimed in claim 1 in which said impregnation is achieved by conducting said fibers through the nip of opposed, spaced rolls, said nip being positioned beneath the surface of a liquid body of said foamable synthetic resin.

7. A method for the preparation of a fibrous glass fabric comprising thoroughly impregnating a yarn consisting essentially of a plurality of continuous glass fibers grouped in a substantially parallel relationship with a foamable synthetic resin by opening said yarn to coat each individual fiber, curing said resin, weaving a plurality of said yarns to form a fabric, and foaming said resin to laterally displace said fibers individually and disperse said fibers throughout a cellular matrix comprising the foamed product of said synthetic resin.

8. A low density extensible fibrous glass yarn consisting essentially of a plurality of strands, each strand being formed of individual continuous glass fibers dispersed in a substantially parallel relationship throughout an elongate substantially cylindrical cellular matrix, said matrix consisting essentially of the in situ foamed product of a synthetic resin coating upon said glass fibers, each of the individual fibers being displaced from the other fibers of the strand by said resin.

9. A yarn as claimed in claim 8 in which said synthetic resin is polyvinyl chloride.

10. A low density fibrous glass fabric consisting essentially of woven warp and weft elements, said warp and weft elements consisting essentially of a plurality of strands, each strand being formed of individual continuous glass fibers dispersed in a substantially parallel relationship throughout an elongate substantially cylindrical cellular matrix, said matrix consisting essentially of the in situ foamed product of a synthetic resin coating upon said glass fibers, each of the individual fibers being displaced from the other fibers of the strand by said resin.

11. A method for the preparation of a fibrous glass fabric comprising thoroughly impregnating a yarn consisting essentially of a plurality of continuous glass fibers grouped in a substantially parallel relationship with a foamable synthetic resin by opening said yarn to coat each individual fiber, curing said resin, plying a plurality of said yarns to form a plied yarn, weaving a plurality of said plied yarns to form a fabric, and foaming said resin to laterally displace said fibers individually and disperse said fibers throughout a cellular matrix comprising the foamed product of said synthetic resin.

12. A method for the preparation of a fibrous glass fabric comprising plying a plurality of yarns comprising a plurality of continuous glass fibers grouped in a substantially parallel relationship, to form a plied yarn, thoroughly impregnating said plied yarn with a foamable synthetic resin by opening said yarn to coat each individual fiber, curing said resin, foaming said resin to laterally displace said fibers individually and disperse said fibers throughout a celular matrix comprising the foamed product of

said synthetic resin, and weaving a plurality of said plied yarns to form said fabric.

13. A low density fibrous glass fabric consisting essentially of woven warp and weft elements, said elements consisting essentially of a plurality of plied yarns, said yarns consisting essentially of a plurality of strands each strand being formed of individual continuous glass fibers dispersed in a substantially parallel relationship throughout an elongate substantially cylindrical cellular matrix, said matrix consisting essentially of the in situ foamed product of a synthetic resin coating upon said glass fibers, each of the individual fibers being displaced from the other fibers of the strand by said resin.

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