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(54) SUPPLY PACKAGES FOR WET-IMPREGNATED MULTIFILAMENT ROVINGS

(71) We, DeSOTO INC, a Corporation organised under the laws of the State of Delaware, United States of America, of 1700 South Mt. Prospect Road, Des Plaines, Illinois 60018, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a supply package from which wet-impregnated multifilament roving can be withdrawn as desired, for instance for use in the production of fibre-reinforced composites.

The production of fibre-reinforced composites has taken on increasing importance, especially since structures of great strength and light weight can be formed. However, the production of such composites has been difficult and expensive, the proportion of resin has been excessive and poor impregnation and detrimental resin flow have been encountered.

The conventional technique has involved the use of fibrous layers impregnated with viscous tacky resin, these being stored between nonadhesive sheets which are removed immediately prior to use. The sticky resin-containing fibrous layer is laid up, usually by hand, and then heat and pressure are used to cure the resin. In some instances polyester resins which cure in the absence of pressure have been used, but these are slow curing and air inhibited. In addition to the cost and lack of reproducibility which characterize hand manipulation, the proportion of resin needed was excessive which increased expense and reduced the strength of the composite. Also, resin flow during the cure adds further complexity.

The art has also attempted to apply the fibres dry, as by winding or braiding dry yarn, and then applying the liquid resin after the fibres were in place. This has often required twisted yarns, and the resin impregnation has been difficult because the fibres are not thoroughly wetted and uniform and complete impregnation has not been possible.

Application of the wet resin to the dry yarn as it is being applied has also been tried, but fibre wetting has often been poor and the mechanical complexities have been excessive.

A significant advance has been the use of preimpregnated roving in which the roving is preimpregnated with a thermosetting resin in a semi-solid form and overcoated with a thermoplastic film. The use of such preimpregnated roving has provided considerable progress, particularly in enabling the use of textile machinery in the application of the preimpregnated roving.

Nonetheless, the goal has been to be able to store and handle a preimpregnated roving with the resin impregnant being in wet condition. With viscous, tacky resin, the impregnated roving could not be removed from a package unless release sheets were placed between the roving strands. With resins of low viscosity, the resin would flow away from the rovings by gravity when the package was stored. Thus, wet storage was not possible heretofore, and it is this previously impractical goal which is the objective of this invention.

Low viscosity curable resin systems, and particularly radiation curable resin systems, are well known, but use of these to impregnate a roving which is to be stored wet has not hitherto been considered possible.

In accordance with this invention, a supply package for wet-impregnated multifilament fibrous roving comprises multifilament roving impregnated with a curable liquid having a tack less than 6 on a Thwing-Albert inkometer at 100 R.P.M. the roving containing the curable liquid in an amount at least sufficient to fill the spaces between the filaments in the

roving but not in excess of a 3:2 ratio by volume of curable liquid to fibre, the impregnated roving being way wound onto a core to provide a crossing angle between the rovings in adjacent layers of at least 10° to provide free volume storage capacity between the angled rovings to accommodate any of the liquid which may run off a roving or be squeezed from it, the supply package being adapted to supply the roving while still wet with the curable liquid in its uncured state. In this way, the wet-impregnated roving can be easily withdrawn from the cylinder as desired.

The curable liquid is desirably of low viscosity which is identified by a room temperature viscosity of less than about 3000 centipoises.

The supply package is normally constituted by a cylinder of wound roving packaged within a liquid-impermeable wrapper, and in preferred practice the curable liquid is curable with actinic (including ultraviolet) light and the wrapper is opaque to actinic light.

The rovings can be wound on a core in conventional fashion, or the wound cylinder can be hollow to provide a centre feed supply package.

Referring more particularly to the fibrous roving, any multifilament roving can be used. The filaments are preferably of great length, but short fibres, e.g. of staple length, can be used. Glass fibres, carbon fibres, natural fibres such as cotton, and synthetic fibres such as polyamide or polyimide fibres, are all useful. These fibres can be sized, if desired, or strengthened with binder particles. The invention is applicable to any multifilament roving and is not dependent on any particular selection. The form of the roving is also secondary. Untwisted rovings are primarily contemplated since these lead to the strongest composites and are most easily impregnated. Nonetheless, some twist is tolerable and while the more twist the less satisfactory, this invention will perform its function regardless of twist. Packages of glass filaments grouped together into an untwisted bundle are described herein as illustrative.

The curable liquid can be any liquid which can be cured in any fashion so long as it possesses, prior to curing a room temperature tack which is quite low, namely, less than 6 on a Thwing-Albert inkometer of 100 R.P.M. Substantially the entire liquid must be curable because a non-porous composite cannot be formed when a significant portion of the liquid volatilizes under curing conditions.

Curable liquids which contain ethylenic unsaturation for cure are particularly contemplated since these are stable and storable, and yet subject to rapid cure, particularly upon subjection to radiation, actinic light radiation being primarily contemplated, though ionizing radiation is also useful, especially where carbon fibres are used which limit penetration of actinic light.

Ultraviolet-curable ethylenically unsaturated liquids are well known, but it is particularly preferred to employ polyacrylates which have been pre-reacted with a small proportion of monosecondary aliphatic amine, especially diethyl amine or dibutyl amine, so as to form an adduct containing residual unsaturation. From the standpoint of the liquid which is subjected to ultraviolet light exposure, it is preferred to have the amine present in an amount of from 0.5% to 5%, more preferably from 1.0% to 4%, of the polyacrylate in the curable liquid, all as more fully described in United States Patent No. 3,844,916. The preference is based on the fact that such polyacrylated systems cure rapidly on ultraviolet exposure in the presence of air to provide good cured properties. However, one can proceed in an inert gas blanket and use heat and/or ionizing radiation to provide the cure.

While actinic light cure is preferred, one can incorporate a free radical polymerization catalyst, such as benzoyl peroxide, into the liquid and cure the system with heat. This heat can be applied radiantly or with an oven, and the heat can be applied as winding on to the form proceeds or after it is completed.

Heat combined with actinic light can be used, either simultaneously with or subsequent to exposure to the latter, subsequent exposure being preferred when the polyacrylate is hydroxy functional and when a minor proportion of a thermally reactive phenoplast/or aminoplast resin (from 3 to 30% based on the total weight of resin) is present.

The invention will be illustrated using triethylene glycol diacrylate pre-adducted with diethyl amine, this adduct being blended with a diacrylate of a diglycidyl ether of a bisphenol.

When light in or near the ultraviolet range is intended to provide the cure, a ketonic photosensitizer such as benzophenone or a benzoin ether will usually be added.

The proportion of liquid on the fibre in the roving can vary considerably, so long as the ratio of curable liquid to fibre does not exceed 3:2 by volume and there is enough to fill the spaces between the filaments in the roving. Confining attention to glass fibre, one can effectively employ from 20% to 35% by weight of resin, balance glass fibre: this yields stronger and less costly fibre composites than does conventional practice where generally larger proportions of resin are required. The same advantage is obtained using other materials, but the proportions by weight will vary since the other materials do not have the

same density as glass.

Way winding is itself conventional and it creates a wound cylinder in which the rovings in each layer are widely spaced and the rovings in adjacent layers cross one another at an angle of at least 10°, preferably at least 15°, so as to provide a free volume storage capacity between the angled rovings to accept any liquid which may run off or be squeezed from a roving. It has been found that the surface tension between the filaments and the liquid impregnant in combination with the open spaces between the rovings effectively prevents the low tack viscosity liquid from flowing away from the rovings.

The wound cylinder may be packaged within a liquid-impermeable wrapper for storage. A simple aluminium foil wrapper is adequate, especially since the opaque foil prevents actinic radiation from activating the ethylenic unsaturation in a photocurable system thereby promoting premature cure and resultant poor storage stability. The wound cylinder can contain a core, such as a cardboard core, or the core can be removed to enable the roving to be withdrawn from the hollow centre of the cylinder which then forms a centre feed supply package.

The illustrative system described hereinafter is excellently stable on storage and yet is rapidly curable on exposure to actinic light near the ultraviolet range in the presence of air.

Withdrawal of the impregnated wet roving occurs easily. The selection of a low tack liquid, as described above, and way winding eliminates the unwinding problem which exists if conventional tacky resinous liquids are used.

Winding of the wet roving into a final fibre composite is itself well known, such winding leaving little free volume so that a non-porous cured product is obtained. The detailed production of the wound and cured composite is not a feature of this invention and is itself broadly known, but it will be appreciated that when the final form is wound, it is desirable to minimize the free volume in the winding to obtain a non-porous cured product. Thus, the winding tension in the case of the final form will normally be greater than that used for the winding of the supply package.

The invention is illustrated in the following Example. All parts and percentages in the Example and elsewhere in the specification are by weight unless otherwise stated.

Example

Parts		
46.76	Diacrylate of diglycidyl ether of bisphenol A (epoxide equivalent weight of the starting diglycidyl ether = 185)	
48.28	Triethylene glycol diacrylate)	
2.65	Diethyl amine	Pre-adducted with
1.77	Benzophenone	one another.

The above components are mixed together to provide an ultraviolet light-curable liquid having a room temperature viscosity (25°C) of 600 centipoises.

This liquid mixture has a tack of 2.4 at 100 R.P.M., (1.8 at 1000 R.P.M.) at 25°C using the Thwing-Albert inkometer and is used for the impregnation of a glass fibre roving by heating the same to 80°C whereby the viscosity is reduced to aid penetration of the roving.

A glass fibre roving designated "ECK 37-15", continuous end roving with epoxy compatible finish, is withdrawn from a centre feed package and is passed over a cylindrical idler roll the lower portion of which is immersed in the hot curable liquid mixture. This idler roll serves to transfer the liquid mixture to the roving which moves at a speed of 72 feet per minute. The take up of liquid is about 30% by weight of the liquid to 70% of glass. As little as about 20% liquid to about 80% glass can be used in performing this invention.

The impregnated roving is wound onto a cylindrical cardboard core having an outside diameter of 3 inches and a length of 11 inches using a travelling take-up which provides 3-way winds with each traverse. This provides a crossing angle of about 30° between the rovings of adjacent layers in the wound package. The winding tension is minimal.

The wound package is sealed within an aluminium foil wrapper.

The impregnated roving is stable within the package and can be unwound therefrom at any time. The liquid impregnant is of low viscosity and flows easily, but it does not flow within the package, so the roving which is withdrawn remains uniformly impregnated. The low tack enables withdrawal without perceptible effort or damage to the roving filaments.

When the impregnated roving is withdrawn, it is transferred directly from the supply package onto a turning form with the adjacent windings being close together and parallel to one another so that there is little free volume on the form. The windings on the form are subjected to ultraviolet light exposure as winding proceeds to produce a cured piece. Winding was at a rate of 135 feet per minute. A 200 watt per inch mercury vapour lamp 12 inches in length and unfocused was used, the lamp being maintained at a distance of 8 inches from the surface being wound. A winding tension of about 5 pounds was used, and a

strong, well cured composite was formed.

Under the same conditions of winding, a speed of 215 feet per minute was used with exposure to a Berkey Technical Co. (U.S.A.) 5 kilowatt "Addalux" diazo or photopolymer lamp being used during winding to achieve satisfactory conversion to a solid composite form. A Xenon Corporation (U.S.A.) 2 kw pulsed xenon arc was also used to convert the wet-wound composite after it was wound. This post conversion was observed to form a solid composite to a depth of about 1/4 inch.

The Berkey diazo lamp generates predominantly visible light (4177 A°) and the photopolymer lamp generates light at predominantly 3650 A°.

WHAT WE CLAIM IS:-

1. A supply package for wet-impregnated multifilament fibrous roving comprising multifilament roving impregnated with a curable liquid having a tack less than 6 on a Thwing-Albert inkometer, at 100 R.P.M. the roving containing the curable liquid in an amount of at least sufficient to fill the spaces between the filaments in the roving but not in excess of a 3:2 ratio by volume of curable liquid to fibre, the impregnated roving being way wound onto a core to provide a crossing angle between the rovings in adjacent layers of at least 10° to provide free volume storage capacity between the angled rovings to accommodate any of the liquid which may run off a roving or be squeezed from it, the supply package being adapted to supply the roving while being still wet with the curable liquid in its uncured state.

2. A supply package for wet-impregnated multifilament roving as claimed in Claim 1 in which the curable liquid has a room temperature viscosity of less than 3000 centipoises.

3. A supply package for wet-impregnated multifilament roving as claimed in Claim 1 or Claim 2 in which the wound core is a cylinder packaged within a liquid-impermeable wrapper.

4. A supply package for wet-impregnated multifilament roving as claimed in Claim 3 in which the curable liquid is curable with actinic light and the wrapper is opaque to actinic light.

5. A supply package for wet-impregnated multifilament roving as claimed in any of the preceding Claims in which the wound core is hollow to provide a centre feed supply package.

6. A supply package for wet-impregnated multifilament roving as claimed in any of the preceding Claims in which the curable liquid comprises a polyacrylate a portion of which has been adducted with a monosecondary aliphatic amine to produce an unsaturated adduct, and a ketonic photosensitizer rendering the liquid curable upon exposure to light in or near the ultra-violet range.

7. A supply package for wet-impregnated multifilament roving as claimed in Claim 6 in which the aliphatic amine is diethyl amine or dibutyl amine and is used in an amount of from 0.5% to 5% of the polyacrylate in the curable liquid.

8. A supply package for wet-impregnated multifilament roving as claimed in any of the preceding Claims in which the filaments of the roving are glass fibres and the liquid is used in an amount of from 22% to 35% of the total weight of the liquid and glass in the roving.

9. A supply package for wet-impregnated multifilament roving substantially as described in the Example.

10. A method of producing a wound fibre composite comprising withdrawing wet-impregnated roving from a supply package as claimed in any of the preceding claims and winding the wet-impregnated roving on a form with the roving in each wind parallel to the roving in the preceding wind to minimize the free volume storage capacity in the composite which is wound, and curing the liquid impregnant.

11. A method as claimed in Claim 10 in which the tension used in winding on the form is greater than that used to prepare the supply package.

12. A wound fibre composite which has been produced by a method as claimed in Claim 10 or Claim 11.

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