

PATENT SPECIFICATION

(11) 1411529

1411529

- (21) Application No. 7539/74 (22) Filed 19 Feb. 1974
 (31) Convention Application No. 351131 (32) Filed 16 April 1973 in
 (33) United States of America (US)
 (44) Complete Specification published 29 Oct. 1975
 (51) INT CL² C08G 16/02
 (52) Index at acceptance



C3R 19DA1 19DA2 19DBX 19P
 B5A 1R14C2 1R14D
 B5N 0526 0528 1704 2704 2728

(54) METHOD OF FABRICATION OF FURAN RESIN BONDED, FIBER REINFORCED ARTICLES

(71) We, THE QUAKER OATS COMPANY, a Corporation organised under the laws of the State of New Jersey, United States of America of, 617 West Main Street, Barrington, Illinois, 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:—

This invention relates to the fabrication of fiber reinforced resin articles, and in particular, to the fabrication of fiber reinforced furan resin articles, for example fiber reinforced furfuryl alcohol resin articles.

Glass fiber reinforced furfuryl alcohol resin articles are well known, and are regarded as being particularly desirable for use as vessels, containers, and other articles requiring a high degree of chemical resistance, high strength and structural stability.

Such articles are commonly made by "hand lay up" techniques, for example. In such techniques, a fibrous reinforcement material, for example, fiber mat e.g. chopped strand mat or woven roving, is embedded in a pre-applied layer of liquid resin on a shaping element. For example, a gel coat of resin, can be applied to a shaping element, and the fibrous reinforcement applied thereto and embedded therein, with a roller, by hand, for example, homogeneously to distribute the liquid resin throughout the fibrous reinforcement and to work out air voids. Liquid resin is then applied to the first ply of fibrous reinforcement, and another ply is worked in. After applying another layer of resin, an additional layer of fibrous reinforcement can be applied, and the procedure repeated as desired. In some instances resin is worked into pre-applied fibrous reinforcement, and in some instances chopped strand mat is used in alternate layers with woven roving, for example.

The present invention provides a method of fabricating fiber reinforced furan resin bonded articles comprising the steps: (a)

applying a catalyzed liquid furan resin binder to a surface; and (b) embedding fiber reinforcement in the layer; said catalyzed furan resin binder comprising a liquid furan resin having homogeneously admixed therein an effective catalytic amount of aromatic or heterocyclic acid chloride selected from those acid chlorides which, when present in said furan resin in an amount sufficient to provide 1% hydrolyzable chloride based on the weight of the resin, will give a gel time between 8 and 120 minutes.

This invention is not directed to that aspect of the fiber-reinforced resin fabrication art known as pre-preg or pre-mix molding. In the pre-preg technique, resin is predistributed on the fibrous reinforcement, typically stored under refrigeration, and eventually pressed against a shaping surface and heat cured. In pre-mix molding, resin, reinforcement and fillers, not in web form are usually prepared by the molder prior to the time of use. This process is also known as bulk molding or dough molding and is used typically in pressure molding fabrication of solid articles, as distinguished from laminates. The shaped mass is heated to trigger the catalyst, e.g. the mold is heated.

For hand lay up work, it is desirable that the viscosity of the liquid resin be low enough to provide ready penetration of the liquid throughout the fibrous reinforcement, and to provide minimum tendency of the resin to remain adhering to the roller or other working tool. When the viscosity is too high, the rollers tend to adhere to the resin in the applied reinforcement material-liquid-resin mass, with the result that the highly viscous reinforcement material-liquid-resin mass can be disrupted or literally torn apart as the roller is withdrawn therefrom. In addition to developing minimal cohesion between the applied fiber-resin layer and the resin-wetted working roller the lower viscosity resins enhance the working-out of air bubbles from the fiber-resin layer.

On the other hand higher viscosities are

desirable inasmuch as less shrinkage is encountered upon cure, and inasmuch as more tolerable exotherms are usually encountered. Relatively high initial viscosity is a characteristic of liquid resins in which the early stages of polymerization have been carried out at least to some extent in a suitable reactor. Naturally, this controlled advancement of the resinification or condensation reaction involves generation and dissipation of whatever exotherm is encountered with that particular degree of advancement. Consequently, the extent of polymerization or condensation which can be encountered after that resin is catalyzed and applied to the shaping element is diminished by the degree to which the precondensation was carried out in a reactor. Hence, more advanced resin, that is, resins having higher viscosity, relatively speaking, are also characterized as exhibiting diminished exotherms during the course of cure of the fabricated article.

In filament winding, a filament is embedded in a resin-wetted mass while a shaping element is rotated at high speeds, for example.

Thus it will be appreciated that the viscosity of the liquid resin, in hand layup and other fabrication of fiber reinforced furan resin, that is, the viscosity at the moment of contact between the resin and fiber, is an extremely important factor in determining the success of the operation.

Hand layup techniques differ dramatically from pre-preg techniques with respect to catalyst requirements. Pre-preg catalysts must remain dormant for long periods of time and are usually activated by elevated temperatures. Hand layup requires fast-curing catalyst and resin mixture, and yet requires a substantial working life. However, using some known furfuryl alcohol resin catalysts, e.g. aniline hydrochloride, an immediate and abrupt increase in viscosity of the liquid resin is encountered. Hence, when such catalyst and liquid resin are admixed, the liquid resin mixture is in a state of rapid and immediate change in viscosity and this abrupt change in viscosity continues during the so-called "bench life". Hence, during the relatively short "bench life", although the resin can be regarded as "workable", the resin is immediately and abruptly increasing in viscosity. Hence, upon being mixed with the catalyst, the resin may be relatively fluid and free flowing and, shortly thereafter, it may exhibit a relatively high viscosity. In heretofore available methods, it has been common for the viscosity of the resin to double upon being catalyzed, and before it is applied to the shaping element.

Moreover, the exotherm encountered in the catalyst-resin pot can be substantial, with the result that the rapid increase in viscosity is aggravated in the pot, and, in some

instances, the temperatures can exceed the temperature at which steam is evolved.

Organic acid chlorides have been generally regarded as extremely fast catalysts and hence unsuitable for fabrication techniques requiring substantial working life.

Use of slowly catalyzed resin mixtures, for example by reducing the concentration of "too-fast" catalysts, has been proposed as an expedient to overcome the high reaction rate of catalysts e.g. aniline hydrochloride, and to provide a "bench life" in which the viscosity of the catalyzed liquid resin is, relatively speaking, stabilized. Such resin mixtures, however, are usually characterized by a more slowly but definitely continuously increasing viscosity with all the advantages of the increasing viscosity. Moreover, at room temperatures the slow reaction rate appears to continue after the so-called "bench life" period of time has elapsed, with the result that low strength, low chemical resistance, and poor strippability is observed in such resin mixtures. In addition, oven curing has been essential for development of physical properties of the fabricated article. However, even after oven curing the low concentration of the "too-fast" catalyst have been found to give insufficient hardness and poor chemical resistance.

A major complaint from fabricators who have used those resin-catalyst mixtures which have a relatively slow cure rate at ambient temperature in the fabrication of hand layup fiber reinforced articles is the fact that such mixtures require the use of ovens, heat lamps, and other similar heating devices to reduce the cure cycle to the extent necessary to facilitate rapid "turnover" of molds and in overall increase in mold production rate of efficiency.

It is an object of the present invention to provide a method of fabricating fiber reinforced furan resin articles, for example furfuryl alcohol resin articles, which is characterized by a working period of time in which the catalyzed resin exhibits relatively stable viscosity.

It is another object of the present invention to provide a method of fabricating fiber reinforced resin articles which is characterized by a relatively fast but controllable room temperature cure rate after the initial working period has lapsed, with the result that the cured article exhibits excellent strippability, high strength, and outstanding chemical resistance.

It is a further object of the present invention to provide a method of fabricating fiber reinforced resin articles in which the fabricator can select a predetermined viscosity liquid resin material in accordance with the particular needs of the particular article being fabricated, and in which the viscosity of the liquid resin will not abruptly

change during the working period of time in which the fibrous reinforcement is being embedded in the liquid resin.

It is a further object of the present invention to provide a method of fabricating fiber reinforced furfuryl alcohol resin articles in which the liquid catalyst and resin mixture has improved "room temperature cure" characteristics, and which does not require the use of ovens, heat lamps, or similar heating devices to reduce cure cycles.

All these and other objects which will be apparent hereinafter are achieved in accordance with the present invention in which the catalyzed furan resin mixture employed comprises, for example, furfuryl alcohol-derived binder having homogeneously admixed therein an effective catalytic amount of a special aromatic or heterocyclic acid chloride. The special aromatic or heterocyclic acid chloride which is contemplated for use in accordance with the present invention includes those aromatic and heterocyclic acid chlorides which, when used in an amount sufficient to provide 1% hydrolyzable chloride based on the weight of the catalyzed resin mixture will give a gel time between 8 and 120 minutes, preferably in the range of 8-40 minutes inclusive. The terms effective catalytic amount, hydrolyzable chloride, catalyzed resin mixture, and gel time, are defined hereinafter. The term effective catalytic amount means that amount of the catalyst which will effectively cure the resin at room temperature to render the laminate strippable within 24 hours. Generally speaking catalyst concentrations herein are expressed as percent hydrolyzable chloride and an amount between 0.5% and 2% inclusive, expressed as percent hydrolyzable chloride, is effective and about 1% is preferred when the contemplated catalysts as defined herein are employed.

The percent hydrolyzable chloride in a catalyst is calculated on the basis of theoretical stoichiometry and on the structural formula of the acid chloride in question. For the purpose of this calculation all the chlorine atoms attached directly to the carbonyl carbon are regarded as hydrolyzable and chlorine atoms attached to a phenylene or other carbon are regarded as being non-hydrolyzable.

As used herein, the catalyzed resin mixture used in the gel time test or fabrication method is the admixture of the special catalyst defined above and the particular resin binder system which is being employed in the particular test or fabrication method. Hence, the catalyzed resin mixture which is used to determine the gel time is the mixture which includes the catalysts, the particular resin binder, including any other additives, modifiers, or impurities, for example, which

would be present in the resin used in the test or fabrication method.

The furan binders contemplated for use in accordance with the present invention and which are used in the gel time test to determine catalysts for use in accordance with this invention include furfuryl alcohol resins, furfuryl alcohol-formaldehyde resins, furfuryl alcohol - furfuryl - formaldehyde resins, furfuryl alcohol - phenol resins, furfuryl alcohol - urea - formaldehyde resins, furfuryl alcohol - urea - phenol resins and furfuryl phenol resins, wherein the resins have a viscosity between 200 cps and 1,000 cps at 25°C. Preferred resins for hand layup have a viscosity between 350-650 cps at 25°C. It is noted that furfural and furfuryl alcohol monomers per se are not contemplated for use as resin binders in accordance with the present invention, although it is to be understood that in a particular resin mixture, substantial portions of the resin binder can include furfuryl alcohol monomer and furfural monomer, e.g. up to about 50% by weight based on the weight of the resin.

Preferred resins are described in Patents 3,594,345 and 3,681,286 issued to Brown and Watson for "Fiberglass Laminates Containing Furfuryl Resin Binder". These preferred resins comprise furfuryl-formaldehyde resin containing formaldehyde-furfuryl alcohol ratio of .25 to 1. Furfural in an amount between 5-25% of the composition is added as monomer after prepolymerization and distillation of the furfuryl alcohol formaldehyde resin.

As used herein, gel time is that amount of time which is required for a 150 gram sample of the resin to which the catalyst has been added at 25°C. to cure to a viscosity of 50,000 cps upon being charged to a paper cup container immediately after admixing of the catalyst and being stirred. A number 358 Dixie (Trade Mark) paper cup or a 8SN Lily (Trade Mark) cup is satisfactory for use in the gel time test. The liquid mass is typically 7/8 inches deep and 3-1/2 inches in diameter at the top during the test in these cups.

A preferred method for determining gel time in accordance with the definition for characterizing catalysts useful in accordance with the present invention involves the use of an automatic gel timer such as, for example, the Randolph Gel Timer-100 (Trade Mark of Shyodu Precision Instrument Co.). This gel timer is a device for determining the gel time of resinous plastics, drying oils, adhesives and two-component elastomers and paints. The apparatus consists of a timer and means for slowly rotating a specially shaped stirrer in a sample mass of resin or elastomer. The rotating means includes a low torque synchronous motor. As viscosity increases, it eventually reaches a level at which

the drag exceeds the torque of the motor. In this preferred embodiment, the stall torque is encountered when viscosity of the test material exceeds 50,000 cps. It is noted that even though the test is carried out at ambient room temperature conditions, typically 25°C. in some samples, the sample temperature will be above 25°C. due to reaction exotherm, at the moment the 50,000 cps viscosity is reached. Starting temperature is precisely 25°C. however. When the motor stalls, the timer is automatically stopped whereupon the gel time can be read directly from the timer by the operator. It should be noted that the rate of cure of the catalyzed resin in the cup is apt to continue to increase with such vigor that the temperature of 100° will be exceeded whereby the water which is generated as a consequence of the condensation reaction of the resins will be converted into steam. Depending on the rate of increase of temperature, this conversion to steam may merely result in an expansion or foaming of the sample resin, or it may result in dangerous spattering of the pot contents. Hence, the technician must take appropriate steps to place the gelling resin sample in a safe location.

We have discovered that, in accordance with the present invention, when the defined heterocyclic or aromatic acid chlorides are used to catalyze the furan resin binder used in hand layup fabrication the viscosity of the resin mixture does not change unduly during the working time until gellation commences to a substantial degree. Thereupon the rate of reaction proceeds at a very fast pace with the result that the laminated form develops sufficient hardness in relatively short periods of time to render the laminated form, for example, readily strippable; and upon further room temperature cure, high strength and chemical resistance, e.g. corrosion resistance, is acquired.

It has been found that those acid chlorides which provide gel times in excess of 120 minutes do not provide sufficient hardness development at room temperature to provide satisfactory strippability.

On the other hand, those acid chlorides which provide a gel time less than 8 minutes have been found to rapidly develop high viscosities and these catalysts present all the disadvantages of the usual rapid cure catalysts for furan resin binders, including, the danger and hazard incurred as a consequence of the exotherm in over catalyzing a mass of furan resin. When these "too fast" acid chlorides are used in lower concentrations in the resins, in order to provide a bench or working life of 10-20 minutes, for example, the resulting article is insufficiently cured, even upon oven cure, to give desired hardness and chemical resistance.

A typical lay up procedure is set forth

below. The following lay up laminate fabrication procedure is used, in accordance with this invention, to determine hardness as reported in the examples. In the test, a Mylar ("Mylar" is a Registered Trade Mark) film is supported on a flat plywood surface. A thin layer of catalyzed resin is applied to wet the film. One layer or ply of 10 mil. (nominal) "C" glass, chemical resistant surfacing veil is applied to the film of resin. This is rolled with a serrated or corrugated roller until the resin pre-coat has thoroughly wet all the glass, all air is removed, and the veil has become embedded in the resin film. Another increment of resin is added and distributed and a one and one-half ounce chopped strand mat ply is added and rolled into and embedded into the resin. This process is continued until the laminate consists of the veil, three plies of chopped strand and finally a second finish ply of veil has been incorporated into the laminate. The cure time starts at the time at which the catalyst is admixed with the resin. It requires about 5 minutes to prepare a 3×5 inch test laminate.

The method of the present invention is not limited to the above procedure, nor is it limited to the use of glass fiber reinforcement, although glass fiber reinforcement is preferred.

As used herein, and in the appended claims, all percents (%), are expressed in percent by weight based on the weight of the composition under discussion, unless otherwise noted, all weights are in parts by weight, and all temperatures are expressed in degrees centigrade.

The following examples are provided for illustration only. Nonetheless, it will be apparent from the following examples that a large number of acid chlorides are not contemplated for use in accordance with the present invention and, indeed, are not suitable for use in accordance with the present invention. In addition to naming a large number of acid chlorides which are contemplated for use in accordance with the present invention, it is possible, in accordance with this disclosure, to determine by means of a simple gel time test, all those acid chlorides which are suitable for use in accordance with the present invention for the purpose of developing readily strippable high strength high chemical resistant furan resin bound, fiber-reinforced articles.

EXAMPLE 1

A furfuryl alcohol resin was prepared as in Example 2 in U.S. Patent 3,594,345 except that the final distillation step is terminated sooner or provide a lower viscosity (e.g. 16,000 cps at 25°C.) whereby dilution with about 25% furfural monomer will provide a final viscosity of about 400 cps. This

resin is then placed in a container in a constant temperature bath until it is precisely 25°C. A one hundred and fifty parts by weight sample of this resin is admixed with an acid chloride in an amount sufficient to provide 1% hydrolyzable chloride based on the weight of the resin. This procedure is repeated to test a large number of respective acid chlorides to determine the gel time. The gel time is determined by placing the 150 grams of the catalyzed resin in an eight ounce capacity paper cup as indicated above, placing a "Randolph Gel Timer-100" stirrer therein, and connecting the stirrer to the Randolph gel timer. The operation of the timer is commenced immediately upon addition of the resin catalyst; and, as soon as the viscosity of the resin-catalyst system exceeds approximately 50,000 cps, the gel timer shuts off automatically. The times observed and the identity of catalysts tested are set forth in Table I below.

TABLE I

	Catalyst	Gel Time (Mins.)	Hardness		
			19 hrs. at RT	24 hrs. at RT	+2 hrs. at 82°C.
25	*Benzoyl Chloride	20.0	80	82.6	39
	O-toluoyl Chloride	4.6			
30	*M-toluoyl Chloride	19.6	78.3	81	43
	*P-toluoyl Chloride	20.2	78.1	79.6	38
	*O-chlorobenzoyl Chloride	9.3	80.3	80.5	38
	*M-chlorobenzoyl	10.5	80.1	81.3	41
	*P-chlorobenzoyl Chloride	14.8	82.8	85	40
35	M-Nitrobenzoyl Chloride	5.5			
	P-Nitrobenzoyl Chloride	4.7			
	*O-Phthaloyl Chloride	8.6	80.8	81.6	45
	M-Phthaloyl Chloride	6.8			
	*P-Anisoyl Chloride	9.9	79.3	80.3	38
40	Cinnanoyl Chloride	2.6			
	Acetyl Chloride	1.0			
	Acryloyl Chloride	3.0			
	Butyroyl Chloride	1.3			
	Lauroyl Chloride	1.8			
45	Pivaloyl Chloride	2.4			
	*2-Furoyl Chloride	11.2			
	Succinoyl Chloride	1.1			
	Adipoyl Chloride	1.1			

* Indicates use of this acid chloride is within definition of invention.

It is apparent from consideration of Table I that none of the nonheterocyclic, nor non-aromatic acid chlorides fall within the gel time definition of catalysts for use in accordance with the present invention.

Moreover, it is apparent from a consideration of Table I that many of the aromatic acid chlorides do not qualify for use in accordance with the present invention. For example, even though m-toluoyl and p-toluoyl chlorides are eminently satisfactory for use in accordance with the present invention, o-toluoyl chloride is not. Also, even though o-phthaloyl chloride is suitable for

use in accordance with this invention m-phthaloyl is not. It was observed that, in addition to causing dangerous and eruptive exotherm in the gel time test pot, those samples exhibiting gel times less than 8 minutes resulted in completely unsatisfactory laminates because of blistering and other heat derived defects. Those catalysts which gave gel times less than 8 minutes were subsequently tested at reduced catalyst levels in the same resin, and it was found that, in each instance, they were unsatisfactory. With respect to attempts to utilize the "Too-Fast" acid chloride, in most instances a catalyst

concentration less than 0.5% in the resin was required to give gel times over 8 minutes. However, these low catalyst concentrations led to insufficient curing, completely unacceptable strippability and completely unacceptable hardness at room temperature cure. Furthermore, elevated temperature cure give inadequate resinification for achievement of necessary hardness and chemical resistance which is otherwise characteristic of furan-derived resin articles. For example, cinnamoyl chloride was too fast, and required 0.25% to give a 20 minute gel time. But, at this catalyst concentration using this catalyst, the laminate developed only 36 (Shore D) hardness after 24 hours at room temperature. After two additional hours at 82°C. it achieved a Barcol hardness of 16. Lauroyl chloride gave comparable results at each of the concentrations discussed above. The data set forth in Table I under "hardness" represents hardness of laminated piece fabricated by hand lay up techniques as set forth above, in accordance with this invention. Hardness values are expressed as Short D hardness, except that those numbers which are underscored represent Barcol hardness numbers. The hardness tests are determined on a laminated article formed by hand lay up in which glass fiber mat is embedded in the furfuryl alcohol binder used in the gel time test as described in the laminate fabrication

procedure set forth hereinbefore and wherein the mat is used in sufficient quantity to provide between 25%+2% by weight based on the weight of the formed, uncured article, e.g. 1 part glass mat and 3 parts catalyzed resin. The hardness values obtained after 2 hours at 82°C. are given to illustrate what is regarded as ultimate or eventual hardness at room temperature.

EXAMPLE 2

A number of respective hand lay up laminated articles are formed using 3 parts of a furfuryl alcohol resin binder used in Example 1, and 1 part of a fiber reinforcement at ambient room temperature conditions using the lay-up procedure set forth above. In separate respective tests 6 chlorides were used in various levels with this resin, e.g. at 0.75% and at 1.5% hydrolyzable chloride levels. The hardness is tested at 24 hours at room temperature, after further curing for 2 additional hours at 82°C., and after still further curing for 1 more additional hour at 100°C., to illustrate eventual or ultimate hardness. The results of these tests are set forth in Table II, in which those numbers having an underscore present represent the Barcol hardness, and those numbers which are not underscored represent Shore D hardness.

TABLE II

At 1.5% (hydrolyzable
chloride) Catalyst

At 0.75% (hydrolyzable
chloride) Catalyst

65

Acid Chloride Catalyst	24 hrs. at RT	+2 hrs. at 82°C	+1 hr. at 100°C	24 hrs. at RT	+2 hrs. at 82°C	+1 hr. at 100°C
Benzoyl	<u>24</u>	<u>48</u>	<u>52</u>	75	<u>37</u>	<u>46</u>
M-Toluoyl	<u>27</u>	<u>48</u>	<u>54</u>	74	<u>38</u>	<u>43</u>
70 P-Toluoyl		<u>42</u>	<u>48</u>			
P-Anisoyl				74	<u>39</u>	<u>48</u>
P-Chlorobenzoyl				75	<u>35</u>	<u>45</u>
O-Phthaloyl				74	<u>39</u>	<u>45</u>

The Barcol scale begins at a reading of about 85 on the Shore D scale. A Shore D hardness rating of 70 is required to give good strippability, generally speaking. The Shore D 70 hardness requirement for strippability is deemed reliable whether a "Mylar" film is to be peeled from the laminate, or whether the laminate will be removed from most intricately shaped practical waxed metal molds, for example. On the other hand, at this state of cure the sheer weight of the article may be so great or the particular

configuration of the articles may be such that it would be undesirable to separate the laminate from adequate physical support until the cure proceeds even further in order to permit the laminate to develop to sufficient structural strength to be non-deformable. However, the gravity-induced deformability is a consequence of the shape and weight of the article, and must be viewed as a factor which is separate and distinct from "strippability".

The data of Table II, even at catalyst

levels corresponding to 0.75% hydrolyzable chloride show that the laminates in accordance with the present invention were readily strippable within 24 hours at room temperature cure.

To assist one in evaluating the data set forth in Table I and Table II herein, it has been found that laminates produced in accordance with the present invention having Barcol value in excess of 30—35 had developed sufficient chemical resistance to pass the traditional acetone wipe test. However, those laminates having Barcol readings in excess of 35—40 are believed near the ultimate chemical resistance characteristic of furan resin-bound articles.

WHAT WE CLAIM IS:—

1. A method of fabricating fiber reinforced furan resin bound articles comprising the steps: (a) applying a catalyzed liquid furan resin binder to a surface; and (b) embedding fiber reinforcement in the layer; said catalyzed furan resin binder comprising a liquid furan resin having homogeneously admixed therein an effective catalytic amount of aromatic or heterocyclic acid chloride selected from those acid chlorides which, when present in said furan resin in an amount sufficient to provide 1% hydrolyzable chloride based on the weight of the resin, will give a gel time (as hereinbefore defined) between 8 and 120 minutes.

2. The method of claim 1, wherein said furan binder is a furfuryl alcohol resin, furfuryl alcohol - formaldehyde resin, furfuryl alcohol - furfural - formaldehyde resin, furfuryl alcohol - phenol resin, furfuryl alcohol-urea-formaldehyde resin, furfuryl alcohol-urea-phenol resin, or furfural-phenol resin, and wherein said binder has a viscosity of between 200 cps and 1,000 cps inclusive at 25° prior to the addition of the catalyst thereto.

3. The method of claim 1 or 2, wherein the fiber reinforcement is a glass strand mat or woven glass fabric and wherein said binder has a viscosity between 350—650 cps inclusive at 25°C. prior to the addition of the catalyst thereto.

4. The method of claim 1, 2 or 3, wherein the acid chloride catalyst is benzoyl chloride, m-toluoyl chloride, p-toluoyl chloride, o-chlorobenzoyl chloride, m-chlorobenzoyl chloride, p-chlorobenzoyl chloride, o-phthaloyl chloride, p-anisoyl chloride or 2-furoyl chloride.

5. A method of any of the preceding claims wherein said applying and said embedding takes place at ambient room conditions, said resin is permitted to cure at ambient room conditions and the resulting cured reinforced resin article is separated from the shaping surface.

6. The method of any of the preceding claims wherein the furan resin binder includes up to 50% by weight of furfuryl alcohol monomer, based on the weight of the resin.

7. The method of any of the preceding claims which comprises repeating steps (a) and (b) until a plurality of plies of the fibrous reinforcement are embedded in the liquid furan binder; steps (a) and (b) being carried out at ambient room conditions; permitting the resultant laminate comprising said plurality of plies embedded in said binder to cure at ambient room conditions and separating the cured laminate from the shaping surface.

8. The method of any of the preceding claims wherein said catalytic amount is an amount of said catalyst sufficient to provide between 0.5 and 2% hydrolyzable chloride by weight based on the weight of the resin binder.

9. A method of fabricating fiber reinforced furan resin bound articles according to claim 1 substantially as herein described.

10. A fiber reinforced furan resin bound article whenever obtained by the method of any one of the preceding claims.

LANGNER PARRY,
Chartered Patent Agents,
Chichester House,
278—282 High Holborn,
London, W.C.1.
Agents for the Applicants.

levels corresponding to 0.75% hydrolyzable chloride show that the laminates in accordance with the present invention were readily strippable within 24 hours at room temperature cure.

To assist one in evaluating the data set forth in Table I and Table II herein, it has been found that laminates produced in accordance with the present invention having Barcol value in excess of 30—35 had developed sufficient chemical resistance to pass the traditional acetone wipe test. However, those laminates having Barcol readings in excess of 35—40 are believed near the ultimate chemical resistance characteristic of furan resin-bound articles.

WHAT WE CLAIM IS:—

1. A method of fabricating fiber reinforced furan resin bound articles comprising the steps: (a) applying a catalyzed liquid furan resin binder to a surface; and (b) embedding fiber reinforcement in the layer; said catalyzed furan resin binder comprising a liquid furan resin having homogeneously admixed therein an effective catalytic amount of aromatic or heterocyclic acid chloride selected from those acid chlorides which, when present in said furan resin in an amount sufficient to provide 1% hydrolyzable chloride based on the weight of the resin, will give a gel time (as hereinbefore defined) between 8 and 120 minutes.

2. The method of claim 1, wherein said furan binder is a furfuryl alcohol resin, furfuryl alcohol - formaldehyde resin, furfuryl alcohol - furfural - formaldehyde resin, furfuryl alcohol - phenol resin, furfuryl alcohol-urea-formaldehyde resin, furfuryl alcohol-urea-phenol resin, or furfural-phenol resin, and wherein said binder has a viscosity of between 200 cps and 1,000 cps inclusive at 25° prior to the addition of the catalyst thereto.

3. The method of claim 1 or 2, wherein the fiber reinforcement is a glass strand mat or woven glass fabric and wherein said binder has a viscosity between 350—650 cps inclusive at 25°C. prior to the addition of the catalyst thereto.

4. The method of claim 1, 2 or 3, wherein the acid chloride catalyst is benzoyl chloride, m-toluoyl chloride, p-toluoyl chloride, o-chlorobenzoyl chloride, m-chlorobenzoyl chloride, p-chlorobenzoyl chloride, o-phthaloyl chloride, p-anisoyl chloride or 2-furoyl chloride.

5. A method of any of the preceding claims wherein said applying and said embedding takes place at ambient room conditions, said resin is permitted to cure at ambient room conditions and the resulting cured reinforced resin article is separated from the shaping surface.

6. The method of any of the preceding claims wherein the furan resin binder includes up to 50% by weight of furfuryl alcohol monomer, based on the weight of the resin.

7. The method of any of the preceding claims which comprises repeating steps (a) and (b) until a plurality of plies of the fibrous reinforcement are embedded in the liquid furan binder; steps (a) and (b) being carried out at ambient room conditions; permitting the resultant laminate comprising said plurality of plies embedded in said binder to cure at ambient room conditions and separating the cured laminate from the shaping surface.

8. The method of any of the preceding claims wherein said catalytic amount is an amount of said catalyst sufficient to provide between 0.5 and 2% hydrolyzable chloride by weight based on the weight of the resin binder.

9. A method of fabricating fiber reinforced furan resin bound articles according to claim 1 substantially as herein described.

10. A fiber reinforced furan resin bound article whenever obtained by the method of any one of the preceding claims.

LANGNER PARRY,
Chartered Patent Agents,
Chichester House,
278—282 High Holborn,
London, W.C.1.
Agents for the Applicants.

