I
Prefoming of wood to bowling pin shape

II
Impregnating bowling pin with (1) impregnant which is polymerizable in situ

III
Polymerizing the impregnant to solid state but preferably not fully polymerizing before adding vapor-imperious sealant coating (2)

IV
Applying and drying sealer coat; may swell completely cured impregnant, or interact with incompletely cured im-pregnant, and then simultaneously cure.

V
Applying relatively thick gel-lacquer protective coating (3), dry.

VI
Apply glossy dirt repellent topcoat (4), dry.

FIG. 4

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The result obtained is a wooden body covered with a hard solid plastic outer shell in which the impregnant plastic has penetrated in a labyrinth manner throughout the pores or openings of the wood texture. When struck, a bowling pin reinforced in this manner is physically much more capable of absorbing blows. It is postulated that the plastic impregnant not only cements and reinforces the wood fibers, but it also serves to distribute the impact energy over a larger depth from the surface as well as spread it over a larger area than the immediate impact area. This is like the foundation of a building, distributing load beyond the immediate surface. The result is that each unit volume of wood absorbs less impact energy.

These two features, namely reinforcement plus deep anchoring, combine to give substantially better service life.

Also of substantial significance according to the invention is the composition and method of application of the sealer coat over the impregnant. By formulating the latter so that it blends preferably by swelling the substrate layer and/or by chemical interaction therewith, an indissoluble bond between the impregnant within the surface of the wooden body and the sealer and subsequent coatings is provided. A nearly unitary structure of wood core and plastic protective shell is produced.

In order that the manner in which these and other objects are attained in accordance with the invention can be understood in detail, reference is made to the accompanying drawings which illustrate the method and product and wherein:

FIGURE 1 is a view, partly in vertical elevation and partly in longitudinal section of a bowling pin produced in accordance with one embodiment of the invention in which impregnant is patterned to greater depth at the base of the pin than at the upper portion.

FIGURE 2 is a fragmentary sectional view, enlarged in scale, taken on line 2—2, FIGURE 1 and showing more distinctly the "graded" effect of the primer impregnant into the wood.

FIGURE 3 is a view, similar to FIGURE 1, illustrating a bowling pin made in accordance with another embodiment of the invention, and

FIGURE 4 is an illustrative flow diagram of successive steps employed in practicing the invention; the invention focuses more specifically on steps II, III and IV.

In order that the method of the invention can be best understood, the general nature of the finished bowling pin will first be described with reference to FIGURES 1—3. FIGURE 1 illustrates one form of pin which can be made in accordance with the invention and which comprises a pin body 10 of maple or other hardwood, the body being impregnated with a synthetic resinous material, as indicated at 20, to reinforce the wood and to provide a superior bond with the composite coating indicated at 3. The impregnant 2 as more clearly shown in FIGURE 2 is graded so that a gradually increased concentration of resin is deposited outwardly from the center of the wood core toward and at the surface of the wood core which essentially is coated with a film of the impregnant. In the embodiment of FIGURE 1, the pin body is impregnated with resin to a greater depth in its base area and throughout an area extending upwardly to a line at 4 at any desired point preferably above the primary ball-impact area, and is impregnated to a lesser depth in all portions of the body above line 4. Alternatively, the pin body can be impregnated to a depth which is uniform over the entire body, as illustrated in FIGURE 3.

An important aspect of the invention resides in the shaded or graduated density of the impregnant, i.e., low density in the deeper portions of the wood and higher density or substantially solid resin at the surface of the wood. This shaded property not only anchors the resin in the wood and prevents separation of the resin coating
from the wood base as occurs with coatings having a sharply defined or distinct separation between coatings, but also provides a cushioning structure to resist the severe blows on the pin by distributing the shock over a larger area of the pin body. A correlative aspect is the employment of a sealer coat over the impregnant, and which is intimately adhered, and which is applied so as to continue the “shaded” property at the bond between these two layers. For this purpose the sealing composition is preferably applied and cured before the polymerization or cure of the impregnant is substantially completed. If desired, a sealant composition containing a minor amount of the resin ingredient of the impregnant may be used to promote this effect. The simultaneous cure as described produces an indistinguishable and inseparable bond between the coating resin layers, i.e., the impregnant and the sealer coats.

Considerably expanded in scale, as compared to FIGURES 1 and 3, FIGURE 2 illustrates the composite coating 3 more in detail. Adjacent the impregnated surface of pin body 1, the coating comprises a relatively thin, substantially vapor-impervious sealing film or coat 5 which is uniformly and tenaciously blended into and bonded to the resinous impregnant and to the wood of the pin body. The sealing film 5 is shown as a separate layer but as will appear in detail hereinafter, the impregnating composition not only extends into the wood body to a substantial depth, advantageously amounting to at least ¼ inch in the ball-impact area, but also forms a continuous but relatively thin film on the surface of body 1 which blends with the sealer coat 5.

In a preferred embodiment, the epoxy resin prime coat is partially swollen by the sealer coat solution composition, causing a substantial blending of the sealer coat into the primer impregnant layer. The sealer composition effectively produces the swelling, or partial solution of the impregnant or a suitable solvent may be employed for this purpose. The co-reaction of the sealer coat composition with the impregnant increases the adhesion between the respective plastic layers. Alternately, it may be desirable that the impregnant resin not be completely cured when the sealer is applied. In this way further curing takes place while the sealer is being dried. It is believed that this results in appreciable chemical reaction between the impregnant and the nitrocellulose sealer coats thus further strengthening the bond between the coats and the resinous shell.

Continuously overlying the sealing coat 5, and uniformly bonded thereto is a relatively thicker protective gel coat 6. This protective coat is then preferably covered by a relatively thin, uniformly adhered dirt-repellent finish coat indicated at 7.

As will be apparent from FIGURE 2, the impregnating synthetic resin material extends for a substantial distance into the pin body 1. In the ball-impact area, it is advantageous to have the depth of the impregnation at least about 0.04 inch, and particularly good results are obtained if this depth is from 0.10 inch to about 0.30 inch. Using compression and vacuum techniques, impregnation of the wood body as high as about 1.2 inch may be obtained where this greater depth is desirable and is considered practical. The sealing film or coat 5 relative to the gel coat 6 is thin but of sufficient thickness and of such composition as to grade into, and make an inseparable bond with, the outermost or surface portions of the impregnant and to provide a vapor-impervious barrier over the impregnant. The sealing coat is generally of the order of 2-12 mils although a thicker film may be employed. The subsequent protective coat is of more substantial depth having a thickness of the order of 25-75 mils although thicknesses up to 250 mils may be employed. The finish topcoat 7 is of conventional thickness, preferably on the order of 2-12 mils but may be increased to as high as 40 mils or more where practical and desirable. It will be understood that

the invention in essence resides in the impregnant and the bond thereof within the wood. Also of importance is the bond thereof with the subsequent sealer coat. The invention is not limited by the application or composition of the "protective" or "finishing" coating used therefor for the purpose of providing a fuller disclosure as regards the preferred practice of the invention.

Having thus generally described the physical nature of bowling pins manufactured in accordance with the invention, the compositions employed will now be discussed in detail.

IMPELLATING COMPOSITION

The invention is based in part upon the discovery that remarkable increases in durability of bowling pins under the conditions of play are obtained by using as the impregnating material a liquid composition containing a polymerizable compound which may be polymerized in situ. The polymerizable composition used as impregnant may contain various additives of the type conventionally utilized in the art to effect various results such as catalysts, curing agents, plasticizers, or organic flexibilizing agents, and the like. The term polymerizable as employed herein is contemplated as inclusive of and generally used interchangeably, where applicable, with reactions described as condensation, curing, drying, polymerization, and molecular association, when used in reference to chemical reactions resulting in extension of molecular size.

Compounds which may be employed as impregnant are the relatively non-viscous materials which may be introduced into the wood core to a substantial degree. Viscosities of the polymerizable impregnant should preferably be below 500 cps. while in the presence of vacuum or pressure impregnation, viscosities below about 100 are advantageous. Included are monomeric as well as partially polymerized compositions preferably those having a relatively low molecular weight.

Impregnating materials which may be employed include resinous compositions characterized as thermosetting as well as thermoplastic. Illustrative examples are such as:

Polyester or alkyd resins which basically are the polycondensation products of dicarboxylic acids with dihydric alcohols and include both saturated polyesters and unsaturated polyesters. The former undergo intermolecular condensation but do not cross-link. Cross-linked with a polymerizable monomer, e.g., styrene, diallyl phthalate, vinyl toluene, methyl methacrylate, triallyl cyanurate, etc. Dihydric alcohols such as glycols of ethylene propylene, 1,3- and 2,3-butylenes diethylene and dipropylene may be reacted with dibasic unsaturated acids such as maleic anhydride or fumaric acid or unsaturated acids such as isophthalic adipic, azelaic or phthalic anhydride. Cure of these is initiated by means of suitable catalyst such as a peroxide or hydro peroxide and an activator or accelerator, e.g., cobalt naphthenate. Optionally these resins, as known in the art, may be modified by 30 to 70% of a suitable drying oil such as coconut, castor, cottonseed, linseed, soy and tung.

Polyvinylidene chloride compositions, using polyvinylidene chloride either as the sole polymerizable material or in combination with a minor amount (e.g., 5-13%) of vinyl acetate. Terpolymers thereof containing 1 or 2% maleic acid or also phenol-formaldehyde resins alone or in blends with polynamides made from dimer acids or with silicone resins.

Acrylic resins, such as acrylate and methacrylate, acrylonitrile (alone or in copolymeric blends with butadiene and/or styrene) ketone resins, silicone-alloy resin, vinyl butyral resins, vinyl chloride, vinyl acetate polymers, vinyl ether resins, vinyl formal, vinyl pyrrolidone and the like.

Particularly advantageous is the class of materials referred to as epoxy resins. Any of the various compounds known as epoxy resins such as the compositions described in U.S. Patent No. 2,633,458 may be used.
Epoxides are manufactured chiefly by the reaction of epichlorohydrin with bisphenol A. Epoxidized novolacs (condensate of phenol with an aldehyde) may also be used and are available commercially. Epoxy resins may also be manufactured by known processes employing peracetic acid. Generally the epoxides contemplated as impregnant are those of the general formula:

\[
\begin{align*}
&\text{O} \\
&\text{CH}_2\text{CH}-\text{CH}_2 \\
&\text{CH}_3
\end{align*}
\]

wherein \( n \) has a value of from 0 to about 7. Those in which \( n \) has a value greater than 7 have increasing viscosity and consequently a diminishing coefficient of impregnation. Expressed alternately suitable epoxy resins are those which have been defined as polymers containing a highly reactive epoxy or oxirane group at each terminal separated by an alternating aromatic and aliphatic system containing hydroxyl groups, are not included by air, have long storage life and cure hard. The epoxy resins are generally hardened or solidified by a variety of curing agents such as various anhydrides, amines, acids, or by another resin for example. Curing agents and amount of this type are well known, see, for example, columns 10 and 11 of U.S. Patent No. 2,872,427.

In using the epoxy resin as impregnant, a solvent or non-solvent system may be used. For an impregnant containing solvents, the curing agent preferably should be slow enough to allow solvent removal from the wood. The ratio of such agent to epoxy preferably varies between 2–25 parts per hundred parts of resin although amounts generally in the range of 0.5% to 30% may be employed. Curing agents may be added before, during or after impregnation with the impregnant, due consideration being given to the amount and kind of curing agent employed.

Illustrative examples of suitable curing agents within the above categories are such as: primary and secondary aliphatic amines, e.g., diethylene diamine, ethylenedi-amine, triethylene tetramine, tetraethylene pentamine; hydroxyaliphatic amines, e.g., N-(hydroxyethyl) diethylene-triamine and N,N'-bis(hydroxyethyl) diethylene triamine; polyalkylene polyamines; acrylonitrile-acrylamide copolymers; acrylonitrile-acrylamide adducts, e.g., cyanoethyl diethylene triamine; aliphatic amine adduct, e.g., an adduct of liquid epoxy resin with an excess of polyamine such as the product of Shell Development Co. available as curing agent "A"; phenolic tertiary amines, e.g., tri(dimethylaminomethyl)phenol; acid anhydrides, e.g., dodecylsuccinic anhydride and methyl "Nadic" anhydride in the presence of a tertiary amine catalyst such as benzyl(dimethyl) amine; benzo trifluoride complexes, e.g., the complex formed by neutralizing BF₃ with an amine which provides a mixture which is stable for long periods of time at room temperature and will cure in 4–6 hours at about 110° C. Reactive flexibilizing agents are used to eliminate brittleness in some epoxy-amine or epoxy-anhydride systems. In referring to flexibilizing agent for the impregnant or flexibilized impregnant, we mean that the impregnant after curing is in a state of increased toughness as distinguished from brittleness. The property of flexibilized resin is such that it has an impact resistance that prevents the wood substrate impregnated therewith from shattering under constrictive forces. For this purpose, polyamide rubbers in combination with an amine may be used. Various commercially available polyamide resins such as those containing amide groups in the polymer structure with or without one or more additional modifying groups such as, amino, cyano, and hydroxy units may effectively be used to function both as curing agent and as flexibilizing agent.

Various aliphatic epoxies such as a diepoxy in which the two aromatic members are bridged by a long aliphatic chain, e.g., 8 to 18 carbon atoms, may also be used as flexibilizers. Aliphatic amines and alkyd diamines, e.g., t-butylamine, hexamethylenediamine, etc., may also be employed. Epoxy compounds of suitably low molecular weight and hence low viscosity are available and may be employed as impregnants without diluents.

When diluents are employed, it is preferred that they be of the type which enter into the epoxy resin forming reaction and upon curing form an integral part thereof. For this purpose various monoepoxides such as allyl glycidyl ether, phenyl glycidyl ether or butyl glycidyl ether blended with a diepoxy to lower viscosity and enhance penetration may be used for example. It is apparent that various other diluents known in the art as suitable for this purpose may be used. Ratios of reactive diluents to diepoxides may generally range from 10% to 50% although the amounts will depend on the nature of the epoxy compound as well as on the diluent itself.

Partial curing as the term is applied herein is understood to mean causing the reaction to take place to such an extent that the polymerization of the impregnant is still incomplete and that further interaction between the impregnant and subsequent applied sealer coat is possible. This is important since it results in a strong bond between the sealer coat and the impregnant. Total cure may then subsequently take place during the application and heating of subsequent coats and during the room-temperature "lay over" of pins prior to lane play.

The following examples in which the parts recited are parts by weight, are provided in order that the invention may be better understood. The examples are illustrative only and should not be interpreted as an indicative of limitations on compositions or conditions stated.

The following general procedure which substantially follows the flow diagram of FIG. 4 may be employed. The details relating to applying protective and finish coatings are presented only as an aid in providing a more complete description and not as a limitation of the invention presented.

Wood cores of proper weight and dimensions are first conveniently supported to facilitate handling such as by inserting dowels therein. The dowed cores are then placed in racks and secured in place. The arrangement is such that preferably throughout the coating process the cores remain on these racks. These racks are preferably fed, in a continuous manner, through the primer-coat units in which the cores are impregnated with the primer solution. The impregnating period varies as desired or as necessitated by conditions or compositions used.

The sealer material is applied to the primed cores. Any suitable means of applying the sealer may be used. Racks of primed, dried cores are fed to the sealer operation where the sealer solution is applied over the primed core surfaces. If more than one coat of sealer is applied, each sealer coat is given an interim drying period.

After proper drying, the sealed cores are readied for application of the gel protective lacquer. A dipping operation is preferably employed. At predetermined timed intervals, the sealed cores are dipped into protective compositions, generally comprising a gel-lacquer solution contained in heated-jacketed tanks and troughs. By a controlled withdrawal rate and by maintaining the gel-lacquer at a constant temperature and viscosity, a uniform coating of desired thickness is achieved. One or more dip applications may be employed. Drying is preferably conducted after each protective coating application. After this coating has dried sufficiently a clear lacquer coating apparatus similar to that used in the sealer application step may be employed to apply a relatively thin topcoat lacquer. The drying is preferably conducted at moderate temperatures, e.g., from about 70°-120° F. for a
minimum period of from 15 minutes to 5 or 6 hours or more.

At this point, the coating operation is complete and various conventional finishing operations may be performed on the coated pins: e.g., dowel removal, bottom facing, stripping, insignia or decal application, weighting, grading and the like. An aging period to effect thorough chemical cure of the plurality of layers comprising the plastic shell may be advisable depending on the treatment used before the pins are applied to lane use.

To test the efficacy of the impregnant prime coat according to the invention in comparison to a surface application obtained by applying a prime coat by conventional means, an atmosphere soak period of 1½ hour was used on the one hand to show the effects of the impregnant in the wood fiber, and application of a prime coat by dipping and by flow coat application on the other hand. The results obtained in Examples 1–4 are summarized in Table 1. In addition, the results of Example 5 showing a more preferred treatment (i.e., longer soak and deeper impregnation), is set forth to illustrate the relatively excellent benefits obtainable according to the teachings of the invention. The data includes examination of micromotated transverse cross-sections in 50 mils depths of coating pins cut to show depth of resin impregnation. The data further reflects useful pin life of the pins, given the basic coatings described in Examples 1–4 and then subsequently coated with the conventional sealer, protective and topcoats by ascertaining rupture and/or separation of the plastic layer from the wood core. The useful life of the bowling pin is considered passed when separation of the plastic coat from the area exceeding three square inches (by usual observation) is reached. Useful life is expressed in terms of lines bowled. Following the prime coat described in Examples 1–5 each of the pins were subsequently similarly coated and examined at room temperature with (1) a 3 mil sealer coat of nitrocellulose 8% solids; (2) a 34 mil titanium dioxide pigmented gel lacquer coating of ethyl cellulose obtained by three dips in the gel lacquer and (3) a 3 mil finish coat of 10.5% solids nitrocellulose.

Example 1

Ten preformed hard maple bowling pin cores are immersed for ½ hour in a 46% solids solution of an epoxide resin comprising 70 parts of the condensation reaction product of epichlorohydrin and bisphenol A (molecular weight 1000–1200); 20 parts of aminoethylene/thalolamine; 3.0 parts of phthalic anhydride—2.5 butylene glycol poly-condensation products; 49 parts of toluene; and 17 parts of isopropanol. The impregnated pins were dried at room temperature overnight.

Example 2

Example 1 is repeated with the exception that three flow coats of the epoxide solution are applied at intervals of 10 minutes. The intervals between coatings are used to dry at a temperature of 95° F. After the third coat the pins were dried overnight at room temperature. The superficial degree of impregnation is reflected by the data obtained for these pins, presented in Table 1.

Example 3

The procedure of Example 1 is repeated with the exception that the “impregnant” comprised a 10% solution of nitrocellulose dissolved in solvent mixture of ethyl acetate, ethanol and toluene, ratio of 2:1:2 respectively. After ½ hour immersion period, the pins were allowed to dry overnight at room temperature.

Example 4

By procedure similar to Example 1, the pins are soaked in a commercially available polyvinylacetate latex. After the ½ hour soak period the pins are allowed to dry overnight.

The inability of the relatively high molecular weight preformed polymeric materials of Examples 3 and 4 to penetrate and form in situ is reflected by the data for these examples in Table 1.

Example 5

40 preformed hard maple bowling pin cores are fully immersed for a period of 4 hours in a 43% resin concentration epoxy polyamide solution of the following composition:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester polyepoxide</td>
<td>90</td>
</tr>
<tr>
<td>Polyamide resin</td>
<td>30</td>
</tr>
<tr>
<td>Toluene</td>
<td>76.9</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>33.5</td>
</tr>
<tr>
<td>2-nitropropane</td>
<td>35.9</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>9.6</td>
</tr>
<tr>
<td>Butyl Cellosolve</td>
<td>3.9</td>
</tr>
</tbody>
</table>

1 Commercially available resin, Shell Chemical Corp.
2 Acrylic polymer commercially available; molecular weight about 10,000 containing about 20–30 mole percent amine units; about 20–50 mole percent amide units and about 20–30 mole percent nitrile units.

The impregnated cores are dried at room temperature overnight and thereafter coated with sealer, gel lacquer and topcoat as Examples 1–4.

Cross sectional segments (50 mils in depth) for each of Examples 1–5 were examined to ascertain impregnant penetration. Examinations were made of the first 50 mils; the second 50 mils and of the 50 mils at the ½ inch or 300 mils point in the transverse section of the bowling pin, the data set forth in columns 1, 2, 3, respectively. In column 4, the average useful pin life before substantial delamination (over an area exceeding 3 square inches) is set forth.

<table>
<thead>
<tr>
<th>Type of pin</th>
<th>Result of examination of the wood at the following depths</th>
<th>Average pin life, games</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>100% of the pores were completely filled</td>
<td>100% of the pores were completely filled</td>
</tr>
<tr>
<td>Example 2</td>
<td>In the first 20 mils depth about 10% of pores had partial filling while an estimated 10% were completely filled.</td>
<td>No filling of pores</td>
</tr>
<tr>
<td>Example 3</td>
<td>No filling of pores</td>
<td>.00</td>
</tr>
<tr>
<td>Example 4</td>
<td>2-3 mils of wood saturation; 10% of pores had partial filling.</td>
<td>.00</td>
</tr>
<tr>
<td>Example 5</td>
<td>100% of the pores were completely filled</td>
<td>100% of the pores were completely filled</td>
</tr>
</tbody>
</table>

* More than 8,000.
In each of the Examples 6-12 dual runs are made; one in which the impregnant is partially cured (as described more in detail in Example 17) and a run in which the impregnant is incompletely cured at the time the successive sealer coat is applied. In such instances the product by the method using the partially cured impregnant was at least equal to and in most instances substantially superior to the pins processed by first fully curing the impregnant before application of the sealer.

**Example 6**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>76.9</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>25.9</td>
</tr>
<tr>
<td>2-nitropropane</td>
<td>35.9</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>7.2</td>
</tr>
<tr>
<td>Butyl Cellosolve</td>
<td>3.9</td>
</tr>
<tr>
<td>Polyether polyepoxide</td>
<td>18.8</td>
</tr>
<tr>
<td>Polyamide resin</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Similar to that of Example 6.

In this formulation, solids content of the solution is 15% by weight and the solvent mixture is of such nature that both good penetration of the hardwood body of the bowling pin and good volatilization of the solvents at normal curing temperatures are attained. The composition is preferably applied to the bowling pin body by soaking the wood body in the liquid composition for a period varying from 1 to 3 hours, depending upon the depth of impregnation desired or by vacuum or pressure impregnation. Although dip coating, flow coating or spray coating procedures may be employed such procedures are less practical and generally must be coupled with auxiliary means for assisting impregnation, e.g., pressure. While the resin system as applied in Example 6 can be cured satisfactorily at moderate temperatures from room temperature to about 200°F., the purpose of heating in many instances is to accomplish residual solvent removal. The resin in the impregnated bowling pin bodies is considered fully cured at room temperature in about 24 hours.

In applying the impregnated composition of this example to the pin bodies to accomplish impregnation of the type illustrated in FIGURE 1, the pin bodies are first immersed base down in the impregnating composition in such fashion that the liquid extends above the primary ball-impact area, such immersion being continued for approximately 2 hours. The pin bodies are then wholly immersed for an additional period of 3 hours. When so treated, a maple bowling pin body absorbs approximately 3.4 ounces of the impregnating composition. The impregnation extends into the bowling pin body approximately 3/8 inch in the primary ball-impact area and about 3/8 to 1/4 inch in the upper portion of the pin. Micrometered cross-sections of the impregnated pin cores aided by suitable staining techniques showed that more than 75% of the resin pick up is contained and distributed below the wood surface. The immersion period may vary substantially depending on composition of impregnant, depth of penetration, etc.

The following example employs an epoxy formulation in combination with a reactive solvent which enters into and forms a part of the resin structure.

**Example 7**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl glycidyl ether</td>
<td>20.0</td>
</tr>
<tr>
<td>Polyether polyepoxide</td>
<td>100.0</td>
</tr>
<tr>
<td>Amine-type curing catalyst 2</td>
<td>24.0</td>
</tr>
</tbody>
</table>

In this formulation, the phenyl glycidyl ether constitutes a solvent or diluent capable of reacting with the epoxy resin, during curing thereof, to produce substantially fully reacted polymeric product. The amine-type catalyst involved also reacts with the epoxy resin, so that the entire composition is reactive to form a cured product. The composition has a relatively shorter pot life than that of Example 6 and hence is advantageously within cure period. The resin pick-up is 3.4 ounces.

In the composition of Example 6, the polyamide resin acts both as a curing catalyst and as a flexibilizing agent, while in the composition of Example 7, the phenyl glycidyl ether, employed as the sole solvent or diluent, is the primary flexibilizing agent. Examination by microtomed analysis shows resin pick up below the wood surface exceeds 80% of the impregnant resin pick-up. The penetration is graded to a depth exceeding 7/8 inch.

The following example is typical for epoxy resin impregnating compositions prepared in accordance with the invention and wherein no diluent or solvent is employed. The lower molecular weight and hence lower viscosity of this epoxy formulation permits suitable impregnation without need for a diluent.

**Example 8**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether polyepoxide</td>
<td>100.0</td>
</tr>
<tr>
<td>Epoxyated cashew nut shell liquid</td>
<td>20.0</td>
</tr>
<tr>
<td>Amine-type curing catalyst 2</td>
<td>22.5</td>
</tr>
</tbody>
</table>

Impregnating compositions of this type can be applied to hardwood bowling pin bodies in various manners. One method which is particularly advantageous, since it makes possible good impregnation in minimum times, is to immerse the bowling pin body in the liquid impregnating composition and apply an elevated pressure to the liquid. Thus, impregnation of the type illustrated in FIGURE 3 can be accomplished by immersing the entire bowling pin body in the liquid resin composition within a suitable pressure apparatus. One piece of equipment is a cylindrical steel container closed at one end by the platen of a standard hydraulic press, the press then being operated to apply a pressure of at least 10,000 pounds per square inch or more over the platen area. Pins so treated with the above impregnant picked up 5.2 ounces in about 30 minutes, over 75% of which is estimated as absorbed below the wood surface. Penetration generally exceeds 3/4 inch.

**Example 9**

Six hard maple bowling pin cores are impregnated by fully immersing for 4 hours in a solution comprising 38.2 parts of toluene disiocyanate, 40 parts of toluene and 40 parts of Cellosolve acetate (tetraethylene grade) in 80 parts of polyol polypropylene glycol. The resin pick up after curing at 120°F. for 3 hours is 4.1 ounces.

Microtomed cross section analysis of the impregnated pins shows that more than 80% of the resin is absorbed below the surface of the wood.

**Example 10**

The procedure for impregnating as in Example 6 (wherein the base of the pin is given a longer soak period) is followed by using the following impregnating composition.

Phenol-formaldehyde resin (mole ratio of phenol to formaldehyde of 1.0/9 not fully reacted) having a viscosity of about 140 cps.

After a total soak time of 4½ hours for the base and 1½ hours for the upper portion of the resin pick-up after cure at 180°F. for 6 hours is about 3.9 ounces. Microtomed analysis shows graded penetration extending 7/8 inch below the wood surface. More than 80% of the resin pick-up is below the wood surface.

**Example 11**

The procedure employed in Example 10 is repeated employing as the impregnant the activated monomeric composition comprising uninhibited styrene containing 0.2% divinylbenzene and 0.1% benzoyl peroxide. Resin pick up is 3.3 ounces. Graded penetration exceeds 7/8.
inch as shown by microtomed analysis. More than 65% of resi
in is below the surface of the wood.

Example 12

The impregnation procedure used in Example 9, where
in the pins are fully immersed, is repeated with the excep
tion that the wood cores are first treated by preheating
and immersed in the impregnant solution. The effect of
preheating is to aid penetration into the wood pore by air
contraction on cooling. The impregnated employment com
prises a solution of undiluted methyl methacrylate acry
lated with 0.08%, based on monomer, of azobisisobutyro
nitrile. The resin pick-up, about 4.1 ounces (over 80% of
which is below the wood surface) as shown by microtomed
examination has penetrated more than 3/8 inch into the wood core.

Example 13

Six hard maple bowling pins were placed in an auto
clave, and the autoclave was then closed and sealed. A
connected vacuum pump was then placed in operation to
reduce the pressure in the autoclave and about the pins
to 3 mm. Hg. and the autoclave and pins were simultane-
ously heated 120° F. After this pressure and temperature
had been maintained for 1 hour, a liquid resin solution
was admitted into the autoclave to a level completely im-
mersing the wood, the solution consisting of:
100 parts of a polyester resin, of maleic anhydride and
propylene glycol; 40 parts styrene and 0.8 parts benzoyl
eroxide.
The vacuum was then removed and the resin solution
was subjected to a pressure of 100 p.s.i. for 60 minutes
following which the pressure was reduced to a vacuum
of 3 mm. Hg for 15 minutes and this cycle was then re
peated three times to force the liquid resin into the pores
of the wood about 9/16 inch throughout its thickness. Next
the resin was drained and removed from the autoclave.
The impregnated pins were placed in an oven and heated
for one hour at 200° F. and at atmospheric pressure to
partially cure the thermosetting resin. Following the cur
ning period, a sealer composition comprising 2 parts ni
trocellulose, 10 parts ethyl cellulose and 1 part polyester
resin dissolved in a solvent system comprising 8 parts of
xylene and 3 parts ethanol. 1 part of dibutyl phthalate
and 0.1 part of commercially available phenylmale
c modified coumarone-indene resin plasticizer, i.e., novolak
is applied as a flow coat on the pins which are then cured
at 250° F. for 3 hours. The effect is to partially swell the
surface impregnant and then fully cure the impregnant
with the sealer partially graded into the impregnant: 3
coats of solvent resistant varnish containing ethyl cellulose
laur lacquer compositions and a final nitrocellulose top
cot of nitrocellulose are applied. The ethyl cellulose
laur lacquer protective coating is applied in substantial
thickness, e.g., about 25-100 mils. The topcoat pro
vides gloss and resistance to dirt pick up.

SEALING COMPOSITION

In general, any conventional lacquer which upon dry
produces an adhering substantially impermeable film
can be employed to provide the sealing coat 5, see FIG
URE 2. This composition must be of such nature that
it provides a uniform and continuous relatively thin film
over the entire impregnated surface of the bowling pin
body, the film being capable not only of bonding chemi
cally to the partially or fully cured impregnating com
position but also of sealing in gases which are entrapped
in the wood of the bowling pin body so that such gases
will not be released during application and curing of the
protective coating 6. In applying sealer to partially cured
wood cores, it is often advantageous to apply a sealant containing a minor amount of resin of
the type contained in the impregnant to aid in pro
ducing a more intimate bond or graded joint between the
two coatings.

Example 14

Ingredient: Parts by weight

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
<td>45.0</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>30.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>15.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.2</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>0.2</td>
</tr>
</tbody>
</table>

1 30 sec. viscosity (ASTM Test No. 301-30).
2 Polymerization product of phthalic anhydride and gly
col of 5.3 butylene.

Advantageously, this composition is applied to the
impregnated bowling pin body, after the epoxy resin im
pregnating composition has been substantially, but not
fully, cured. Application of the sealing material is ef
ected in multiple stages if desired and by any of the
known coating techniques. In the present run three flow coats are applied, the product being dried for 30 minutes
at 100° F. after the application of each coat.

A variety of other sealer compositions in lieu of nitro
cellulose may be employed such as blends of nitrocel
lulose and various ethers, e.g., cellulose ether. Known
plasticizers such as dibutyl phthalate may also be incor
porated in the sealer composition. As noted herein
above, the sealer coat may contain a minor proportion
of resin of the type forming the resinous base of the im
pregnant. A sealer blend of this type when applied to
an incompletely cured primer-impregnant produces an
indistinct or blended bond between the impregnant and
sealer to which the subsequent coatings have poor
anchorage. The character of the bond is such that it
substantially minimizes the possibility of delamination
from the wood substrate.

PROTECTIVE COAT COMPOSITION

The protective coat 6 is of substantial thickness and
generally comprises a plurality of layers of any one of var
ious compositions known for this purpose. Preferably a
composition providing a relatively thick coating with each
application is used. Various formulations are available
commercially for this purpose. They are generally ap
plied by hot dip procedures. Coatings varying from about
3 mils to about 30 mils for each dip are obtained
in this manner. Examples of suitable protective coat
ings include various gel lacquers, e.g., ethyl cellulose,
cellulose acetate butyrate, generally containing suitable
pigmentation such as titanium dioxide and plasticizer
such as diocyl phthalate, dibutyl phthalate, etc. Ethyl
cellulose gel Lacquers are particularly advantageous.
A protective coat comprising multiple applications of ni
trocellulose lacquer solutions may also be employed for
this purpose. The following example is typical of gel lac
quers that are useful and can be applied over the sub
strate prepared in accordance with the invention.

Example 15

Ingredient: Parts by weight

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl cellulose</td>
<td>316.0</td>
</tr>
<tr>
<td>Xylene</td>
<td>610.0</td>
</tr>
<tr>
<td>Ethylcellulose glycol monothyl ether</td>
<td>278.0</td>
</tr>
<tr>
<td>Petroleum naphtha</td>
<td>222.0</td>
</tr>
<tr>
<td>Titanium dioxide pigment</td>
<td>7.0</td>
</tr>
<tr>
<td>Alkyl plasticizer</td>
<td>7.0</td>
</tr>
</tbody>
</table>

1 100 cps. medium ethoxy.
2 See note 2 for Ex. 14.

This composition is applied to the impregnated bowling
pin body by dipping the body in the lacquer composition.
while maintaining the lacquer composition at approximately 200°F, the bowling pin body then being withdrawn at a controlled rate over a 5-minute cycle, although this cycle is not critical. The dipping operation is repeated three times (although more or less dips may be suitable). Preferably the multiple layers should provide a coating of at least 25 mils thickness. The pins are dried for 2 hours at 110°F, after each of the first two dips, and for 1½ hours at 180°F, after the third dip.

The particular solvent composition employed in this example is so prepared as to provide for slight dissolution or swelling of the nitrocellulose of the sealing film, so that the protective coat 6 is more securely adhered to the sealing film. The sealing film, as noted hereinbefore, is vapor-imperious, and precludes escape of gases from the bowling pin body during establishment of the relatively thick protective coating; it therefore makes possible a uniform, uninterrupted protective coating of very substantial thickness.

**TOP COAT COMPOSITIONS**

Any conventional lacquer suitable for providing an attractive, glossy, dirt-repellent top coat can be employed for coat 7. As such example compositions comprising polyurethanes, polycarbonates, acrylics, vinyls, shellac, polystyrene, and the like may be employed and modified, where desired, with suitable solvents, plasticizers etc. Advantageously, a composition containing a conventional nitrocellulose base is used. Compositions such as the following for example provide excellent top coats.

**Example 16**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
<td>6.25</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>8.25</td>
</tr>
<tr>
<td>Toluene</td>
<td>51.25</td>
</tr>
<tr>
<td>Isobutyl acetate</td>
<td>25.12</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>21.25</td>
</tr>
<tr>
<td>Ethanol</td>
<td>10.00</td>
</tr>
<tr>
<td>Butanol</td>
<td>6.25</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>0.31</td>
</tr>
<tr>
<td>Castor oil</td>
<td>0.31</td>
</tr>
</tbody>
</table>

1. 3½ sec. viscosity
2. 9% sec. viscosity

Such compositions are applied by flow coating followed by drying at 30 minutes at approximately 100°F, although dip or spray coating techniques and/or air drying of the coated pin may also be employed. The following example is typical of the present method when the epoxy resin impregnating composition includes a volatile solvent medium.

**Example 17**

Hard maple bowling pin bodies were preformed in a conventional manner to the desired dimensions. Preferably the pin bodies are suitably supported and racked for multiple handling. An epoxy impregnating composition was prepared in accordance with Example 6 and maintained in an open soak tank equipped with heat exchanger coils, the liquid impregnating composition being maintained constantly at 70-72°F throughout the impregnating operation. The maple bowling pin bodies were maintained submerged in the liquid impregnating composition for 3 hours and were then removed and placed in a drying rack and dried at room temperature for 24 hours. The extent of cure of the epoxy resin material after this period is such that it is materially less than complete, but adequate to convert the film of resin composition on the surfaces of the bowling pin bodies to a solid condition. The nitrocellulose sealer lacquer of Example 14 containing in addition 15% by weight based on the nitrocellulose, of epoxy polyamide resin, is employed as the sealer. The bowling pin bodies were given 3 coats of this lacquer by conventional flow-coating procedures, the pin bodies being dried for 1½ hour at 150°F, after each flow coating stage. The resulting sealing coat was approximately 4 mils in thickness and was uniform, fluid-imperious and extended continuously over the entire pin body. The sealing coat was uniformly and tenaciously bonded to the epoxy resin material at the surface of the pin body, further curing of the epoxy resin of the impregnant primer coat having occurred during application of the sealing coat. Microscope examination of microtomed layer cross-sections shows the graded bonded between layers.

A protective coat of ethylcellulose gel-lacquer containing epoxy polyamide resin, 10% based on weight of ethylcellulose, and a minor amount of a solvent mixture comprising toluene, ethyl acetate, and ethanol to promote fluidity was then applied to each bowling pin body by dipping the same three times in the gel-lacquer composition to give a protective coat about 40-45 mils. In this operation, the pins were initially at room temperature and the gel-lacquer composition was maintained at 200°F. After each of the first two dips, the bowling pin bodies were dried for 1 hour at 120°F. After the third dip, they were dried for an additional 2 hours at 150°F. The finished protective coat was completely uniform and free from any imperfections normally encountered because of escape of gases from within the pin body.

The bowling pins were then completed by applying a top coat, using the formulation of Example 16 applied by a conventional flow-coating procedure and then air-dried at room temperature for 30 minutes. A top coat of 2-4 mils thickness is applied although a coating up to 15 mils by multiple applications may be suitably applied where desirable.

Randomly selected, samples of the bowling pins so made were subjected to repeated impacts on a laboratory impact testing apparatus, the tests being continued until the pins had been subjected to 12,000 cycles of blows on the impact tester representing approximately 1800 lines of actual rough bowling alley service. The test pins were then observed to be substantially free of hair-line cracks in the composite coating, having excellent surface appearance, exhibited little loss of coating material and little change in ball-line diameter.

The excellent results of a finished pin structure using the wholly reactive impregnant composition described in Example 8 is illustrated by the following example.

**Example 18**

The procedure of Example 17 was repeated, except that the impregnating composition of Example 8 was employed. The manipulative conditions for the impregnating step were the same as in Example 17 and application of the sealing coat, the protective coat and the top coat was accomplished as described in Example 17. Test pins selected at random were tested on the same laboratory impact test apparatus until the test pins had been subjected to 15,000 cycles of blows, equivalent to more than 2000 lines of rough bowling alley service. Upon inspection the pins were found to have no hair-line cracks, no loss of coating material and even less change in ball-line diameter and separation of coating material from pin wood bodies than was true for the test pins of Example 11. No plastic-coated, wood body bowling pin is known which has survived such a severe life test without extensive damage. It will be apparent to those skilled in the art that the present method can be modified in various ways without departing from the scope of the invention. Where it is desirable to accomplish extensive impregnation more quickly, the wood bowling pin bodies can be heated prior to being immersed in the impregnating liquid, the resulting cooling of the pin bodies producing a "vacuum effect" by reason of condensation of vapors in the pores.
of the wood, so that impregnation is enhanced. Other types of vacuum impregnating procedures can be employed with similar effect. Conversely, impregnation can be accomplished under elevated pressures, so that deeper short-time penetration of the epoxy resin material results in the case of simple soaking. The general method outlined in FIGURE 4 is describing the invention may be modified by employing multiple applications of the epoxy resin compositions. As a typical example, the hardwood bowling pin bodies can first be treated, by a vacuum dip-impregnation step, with a solution compounded generally in accordance with Example 5 but having a relatively low solids content, on the order of about 5-10% by weight, the epoxy resin material so applied then being partially cured, and a second application of a similar epoxy resin solution of higher solids content, on the order of from about 15%-50% by weight, for example, can then be applied by flow coating procedures. The second application of epoxy resin material, which may contain minor amount of a high molecular weight material such as nitrocellulose, is then partially cured and a relatively thick protective coating applied, by dip-coating procedures, using the ethylcellulose gel-lacquer composition of Example 14. In this modified embodiment, the second application of epoxy resin blend is substituted for the nitrocellulose sealing coating provided in Examples 16 and 17.

From the foregoing, it is apparent that the invention provides a much improved bowling pin characterized by having a superior bond, that provides between coating layers and particularly between the wood surface and resinous coatings, a graded interlayer penetration extremely resistant to delamination.

It is postulated that this "graded joint" construction helps dissipate impact energy to a larger area, depth, and volume of the wood core, therefore lessening the intensity of impact received by each unit volume of wood. This feature, together with the higher wood reinforcing action offered by high degree of impregnation offered by the use of low M.W. impregnant, high impact strength of the resin-wood combination, and the excellent adhesion of this primer to subsequent sealers and protective coats, combine to give a pin of much longer service life than has heretofore been known in the art.

We claim:

1. The method of encasing a wooden bowling pin body in a plastic protective cover comprising impregnating said body to fill the pores to a depth of at least 0.04 inch with a liquid epoxy resin composition which has a consistency capable of permeating said body and is polymerizable in situ, at least partially polymerizing said composition and thereby converting said composition to solid composition anchored as an integral structure in said wooden body, and thereon applying to said bowling pin body a vapor impervious resinous film and drying the same to provide a sealing coat uniformly and tenaciously bonded to the solidified resin impregnating composition and a synthetic resin protective layer.

2. The method of encasing a wooden bowling pin body in a plastic protective cover comprising impregnating said body to fill the pores to a depth of at least 0.04 inch with (1) a liquid epoxy resin composition which has a consistency capable of permeating said body and is polymerizable in situ, at least partially polymerizing said composition and thereby converting said composition to a solid composition anchored as an integral structure in said wooden body; thereafter applying to said bowling pin body a vapor impervious coating (2) comprising a resinous lacquer and drying the same to provide a sealing coat uniformly and tenaciously bonded to the resin of said solidified composition (1) and subsequently applying and curing thereon a resinous protective coating (3) and a dirt-repellent resinous topcoat (4).

3. The method of claim 2 wherein the epoxy resin composition (1) is not fully polymerized prior to application of said lacquer coating (2) and wherein said coating (2) comprises a nitrocellulose base, and complete polymerization of the epoxy resin composition (1) is effected simultaneously with the drying of the lacquer coating (2).

4. The method of encasing a wooden bowling pin body in a plastic cover comprising impregnating said body to fill the pores to a depth of at least 0.1 inch with (1) a liquid composition comprising a curable epoxy resin blend having a curing agent and in addition providing on the surface of said bowling pin body a continuous film of said liquid impregnating composition, at least partially curing said epoxy resin and thereby converting said continuous film to solid form, thereafter applying to said bowling pin body a coating (2) of a synthetic resinous lacquer and curing the same to provide a sealing coat uniformly and tenaciously bonded to the resin of said solidified composition (1) and subsequently applying and curing thereon (3) a protective synthetic resin gel-lacquer protective coating and (4) a dirt-repellent synthetic resin topcoat.

5. A method in accordance with claim 4 wherein the protective coating (3) is a pigmented ethylcellulose lacquer.

6. The method of claim 4 wherein said liquid resin composition (1) is a solution of epoxy resin in a volatile organic solvent medium, said solution containing as the curing agent for the epoxy resin an anorganic nitrogen compound and having a solids content of at least 5%, and curing of said epoxy resin is effectuated by maintaining the impregnated bowling pin body at a solvent-vaporizing temperature not exceeding 200°F.

7. The method of claim 6 wherein said organic nitrogen compound is a polyamide resin.

8. The method of encasing a wooden bowling pin body in a plastic protective cover comprising impregnating said body to fill the pores to a depth of at least 0.1 inch in the ball-impact area, with (1) a liquid curable epoxy resin composition and providing on the surface of said bowling pin body a continuous film of said liquid impregnating composition, partially curing the epoxy resin composition and thereby converting said film to solid form, applying to said impregnated body (2) a nitrocellulose lacquer to form a sealant for the epoxy composition drying the same to provide a substantially vapor-impervious barrier uniformly and tenaciously bonded to the cured epoxy resin of said first-mentioned film, applying to said sealant coat an ethylcellulose gel-lacquer coat (3), drying said ethylcellulose lacquer to provide a protective coat having a thickness which is from about 25 to 250 mls uniformly bonded to said sealing coat and applying and drying a nitrocellulose topcoat (4) over said gel-lacquer coat.

9. The method of claim 8 wherein said epoxy resin composition is a solution of epoxy resin in a volatile organic solvent medium, said solution having a solids content of at least 5% and containing a polyamide resin as a curing catalyst.

10. A bowling pin comprising a preformed hardwood body in which the pores are impregnated with (1) a liquid epoxy resin polymerized in situ, to a depth of at least 0.1 inch, said impregnated body being coated respectively with (2) a substantially vapor-impervious sealing film of synthetic resin of a thickness not more than 15 mls (3) a nitrocellulose gel-lacquer coat of between about 25 and 250 mls thickness and a dirt-repellent lacquer coating of a thickness not more than 10 mls.

11. A bowling pin in accordance with claim 10 wherein the synthetic sealing film (2) comprises nitrocellulose lacquer.

12. A method in accordance with claim 10 wherein the synthetic sealing film (2) comprises nitrocellulose lacquer.
has a consistency capable of permeating said body and is polymerizable in situ.

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<th>Date</th>
<th>Inventor(s)</th>
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<tr>
<td>3,030,249</td>
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<td>Schollenberger et al.</td>
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