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(54) Title: QUICK-CURE GAME BALL COATING SYSTEM

(57) Abstract: A fast-curing polyurethane coating system for a game ball is described herein. The coating system comprises a mixture of a polyol, an isocyanate, a functional silicone additive, a solvent and a surprisingly high level of catalyst which accelerates the curing process. The coating is a two-part polyurethane system which is preferably applied by spraying. The coating is particularly well-suited for use on golf balls, and also can be applied to other game balls such as softballs, baseballs, and cricket balls.

QUICK-CURE GAME BALL COATING SYSTEM

Cross Reference to Related Applications

This application is a continuation-in-part of Application Serial No. 08/609,822, filed March 1, 1996.

Background of the Invention

The present invention relates generally to game balls, and more particularly to a quick-cure coating for game balls.

For decades, golf balls were finished by applying one or more coats of paint or the like to the outer surface of a golf ball cover. To achieve a desirable white appearance, a multicoat paint system typically comprising a primer coat followed by one or more opaque coatings was applied to the golf ball. Such golf balls are typically referred to as "painted balls". In the 1980's, the concept of incorporating pigment into the cover material prior to molding the cover of the golf ball was introduced, thereby eliminating the step of painting the golf ball. Such golf balls are typically referred to as "pigmented balls".

Whether the golf balls are painted or pigmented, identifying indicia such as the manufacturer's trademark or logo, or a model or identification number, are stamped on the ball. In order to prevent the stamped indicia from being rubbed off, and also to impart a desirable glossiness to the ball, one or two clear outer coatings are applied to the ball. Typically, such clear coatings consist of a clear solvent based primer or water borne primer followed by a clear urethane top coat. The logo or other indicia typically is stamped on the primed ball before application of the top coat. The urethane top coat is usually a two-part polyurethane, consisting of a polyol and a polyisocyanate or polyisocyanurate with at least two $-N=C=O$ groups mixed together and reacted to form the urethane coating.

In golf ball manufacturing, the period of time required to apply and cure the final glossy top coat encompasses a large percentage of the total time required for golf ball manufacture. Known golf ball finish coatings typically require 6 - 8 hours of curing at an elevated temperature. Curing is generally conducted in a batch-type manner in large ovens.

One advantage of the conventional method for finishing golf balls is that the long cure time of the final top coat ensures that adhesion of the finish coating to the golf ball is strong, and as a result, the golf ball has a long, useful life. Another advantage is that the pot life of the mixed coating is relatively long. However, known methods are disadvantageous in that the 6 - 8 hour curing time prevents same day delivery of golf balls, particularly customized logo balls. Furthermore, one or more very large ovens are required if a sizable number of golf balls are to be manufactured daily.

In a conventional polyurethane finish coating system for coating golf balls, a polyol and a polyisocyanate or polyisocyanurate with at least two $-N=C=O$ groups are mixed in a pressure pot without a catalyst. The mixture in the pressure pot is then sprayed on the outer surface of the golf balls. Most of the mixture remains in the pot for some period of time before spraying. Thus, it is important to include enough solvent in the coating mixture to prevent the coating mixture from curing while it is still in the pressure pot and to provide for acceptable flowout of the coating mixture. However, it would be environmentally beneficial to be able to reduce the quantity of solvents in the coating system.

Summary of the Invention

An object of the invention is to provide a fast curing coating system for game balls, such as golf balls, softballs, baseballs, cricket balls and the like.

Another object of the invention is to provide a game ball having a fast curing coating that demonstrates adhesion and abrasion resistance which is comparable or superior to prior known urethane coatings.

Yet another object of the invention is to provide a game ball coating system having a high solids concentration.

Yet another object of the invention is to provide a low V.O.C. coating system for a game ball.

Yet another object of the invention is to provide a game ball having a fast curing coating that demonstrates adhesion and abrasion resistance which is comparable or superior to prior known urethane coatings and also has a low coefficient of friction.

Yet another object of the invention is to provide a game ball coating system having opacity if desired.

Other objects of the invention will become apparent from the following description.

The invention in a preferred form is a game ball coating system comprising a mixture of a polyol, at least one of a polyisocyanate with at least two $-N \equiv C=O$ groups and a polyisocyanurate with at least two $-N=C=O$ groups which is present in a quantity appropriate to provide an equivalent weight ratio of $-N=C=O$ to $-OH$ in the range of 0.90 to 1.8, up to 70 wt % of a solvent, a functional silicone additive, and a compatible catalyst. The catalyst is present in a quantity such that the coating composition will be cured to a Sward rocker hardness of at least 10 in less than about 1.5 hours at an elevated temperature, preferably less than 30 minutes, more preferably less than about 10 minutes. The quantity of catalyst is preferably sufficient to provide for an at least 100% increase in viscosity of the coating system within 30 minutes at 25°C, 1 atm and 60% relative humidity.

When applied to a game ball, the polyurethane finish coating preferably has an average initial wet thickness of no more than about 3.5 mils. In a particularly

preferred form of the invention, the coating system is a two-part system including a first part containing the polyol, the catalyst and at least a portion of any solvent which is used, and a second part containing the polyisocyanate and/or polyisocyanurate. The functional silicone additive may be added to either part as long as it is compatible. Preferably, the functional silicone additive is added to the polyol portion.

The polyol preferably comprises at least one of a polyester, polyether or acrylic, and has a hydroxyl equivalent weight of 50 - 1500, and more preferably 100 - 1000.

Blends of different polyols can be used. More preferably, the polyol is a saturated polyester polyol, and most preferably is the reaction product of an organic acid which includes at least one member selected from the group consisting of adipic acid, phthalic acid and isophthalic acid, an anhydride, and a glycol which includes at least one member selected from the group consisting of ethylene glycol and trimethylol propane.

The polyisocyanate or polyisocyanurate with at least two $-N=C=O$ groups preferably includes at least one member selected from the group consisting of biurets and isocyanurate trimers of hexamethylene diisocyanate. Blends of polyisocyanates and/or polyisocyanurates can be used. The solvent preferably includes one or more members selected from the group consisting of ketones, esters and acetates.

The catalyst preferably comprises at least one member selected from the group consisting of a zirconium complex, dibutyl tin dilaurate, dibutyl acetylacetonate, dibutyl tin dibutoxide, dibutyl tin sulphide, dibutyl tin di-2-ethylhexanoate, dibutyl tin (IV) diacetate, dialkyltin (IV) oxide, tributyl tin laurylmercaptate, dibutyl tin dichloride, organo lead, tetrabutyl titanate, tertiary amines, mercaptides, stannous octoate, potassium octoate, zinc octoate, diaza compounds, and potassium acetate. The catalyst preferably is present in a quantity of 0.01 - 10 weight % active catalyst (not including any carrier) based on total resin solids (polyol plus polyisocyanate or polyisocyanurate, excluding solvents). The quantity of catalyst will depend upon the

type of catalyst, polyol, polyisocyanate or polyisocyanurate, and solvents which are used, as well as the curing temperature and desired curing time. When dibutyl tin dilaurate is used as the catalyst, it preferably is present in an amount of about 0.05 - 0.35 weight % active catalyst based upon total resin solids, and more preferably 0.08 - 0.15 weight % based upon total resin solids. Excellent results have been achieved using about 0.1 weight % dibutyl tin dilaurate based upon total resin solids.

Other catalysts preferably are used at levels which will produce the same state of cure as 0.05 - 0.35 weight % or more preferably 0.08 - 0.15 weight % active dibutyl tin dilaurate. The catalyst preferably is present in an amount sufficient to reduce the curing time of the coating by at least about 75% as compared to a coating system which does not contain the catalyst but is otherwise identical. When a zirconium complex is used as the catalyst, it preferably is present in an amount of about 0.05 - 10 weight % active catalyst based upon total resin solids, and more preferably 0.1 to 2 weight % active catalyst based upon total resin solids.

Optionally, if desired, the coating system may contain a pigment, preferably a white pigment, to make the coating more opaque. The amount of pigment used varies depending on factors such as the particle size, the particular pigment, and the amount of opacity desired.

The invention accordingly consists in the features of construction, combination of elements and arrangement of parts which will be exemplified in the construction hereafter set forth and the scope of the application which will be indicated in the appended claims.

Detailed Description of the Invention

The invention is a coating system which will form a highly durable polyurethane coating on a game ball. The coating system contains an amount of catalyst which far exceeds the quantity of catalyst recommended by polyurethane coating

manufacturers. When the high level of catalyst is used in conjunction with the mixing parameters of the invention, an excellent game ball coating can be formed at a surprisingly fast rate. By using an unexpectedly large amount of catalyst in the coating system, continuous production is facilitated. The coating system of the invention also provides for the uniform application of a game ball coating on a dimpled game ball such as a golf ball in which minimal dimple flooding occurs.

The coating system of the invention can be used for application of primer and/or top coatings, and is particularly useful as a finish coating system for a game ball. When the coating system is used to form a final top coating, the coating can be applied to game balls which have a variety of types of primer coatings, including waterborne and solvent-borne polyurethanes, and epoxies.

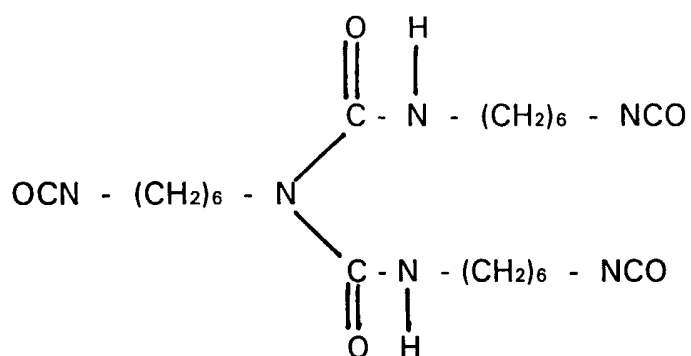
The final coating can be applied to a primed ball after the primer has been cured under conditions sufficient to drive off 90 - 98% of the water and solvent in the primer coating system, e.g. after the primed ball has been in a dry oven at 150°F for about 10 minutes. Furthermore, the coating of the invention can be applied as a final top coating directly to a game ball cover, without the use of a primer coating, when the particular coating system which is used provides for sufficient adhesion to the game ball cover without the use of a primer. In eliminating the primer coating, it is important to take into consideration the difficulty in adhering polymer coatings to certain game ball covers, such as golf ball covers which are made of ionomers or blends of ionomers with other cover materials, due to the presence of olefins in the ionomer. Thus, in some cases, it may be beneficial to treat an unprimed ionomer-containing cover before applying the top coat in a manner appropriate to promote adhesion. For game balls with a cover made of an ionomer having a relatively high zinc content, a thermoplastic polyurethane, or mixtures of ionomers and polyurethanes, it is likely that neither a primer coat nor treatment of the unprimed cover is necessary if the correct top coat is used.

Typically, the average thickness of the final coating is about 0.3 to 2.5 mils after curing, and preferably is about 0.3 - 2.0 mils after curing.

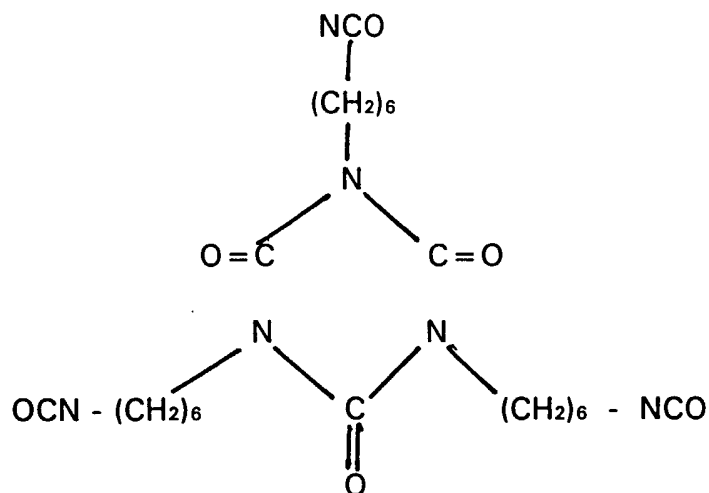
The coating systems of the present invention are two-part coatings with a first part comprising a polyol and a second part comprising a polyisocyanate with at least two $-N=C=O$ groups or a polyisocyanurate with at least two $-N=C=O$ groups. The polyols include acrylic, polyether and polyester polyols as well as alkyds. One particularly preferred coating system according to the invention is a two part solvent-borne polyurethane system in which the first part comprises a hydroxyl functional polyol having an hydroxyl equivalent weight in the range of 50 to 1500, with the most preferred equivalent weight being 200 to 800. Preferably, the hydroxyl functional polyol is ethylenically saturated. Suitable saturated polyesters for use herein include poly (oxydiethylene adipates) that are condensation products of diethylene glycol and adipic acid, branched with trimethylolpropane or pentaerythritol, and polycaprolactone (hydroxycaproic acid) polyesters. Suitable saturated polyethers include polymers of propylene oxide or propylene oxide/ethylene oxide. Such materials are usually triols or diols with molecular weights between 1000 and 7000. Suitable saturated acrylics include derivatives of acrylic acid, such as methyl methacrylate, co-polymerized with hydroxyl functional monomers, such as 2-hydroxy-ethyl methacrylate. Suitable (non-limiting) examples of polyols include Desmophen 651A - 65, 800, 670A - 80, 680 - 70 and 631A - 75, which are saturated polyester resins, available from Bayer Corp., Aroplaz 1133-X-69, a short oil alkyd marketed by Spencer Kellogs Products Div., Reichhold Chemicals, Inc., Minneapolis, MN, Pentalyn 802A, a phenolic modified polyester resin marketed by Hercules Inc., Wilmington De, and VMCA, a hydroxyl functional vinyl resin marketed by Union Carbide, Danbury, CT.

As indicated above, in addition to a polyol, the two-part polyurethane system comprises a crosslinking agent which is polyisocyanate and/or polyisocyanurate with at least two $-N=C=O$ groups and which preferably is carried in a solvent. Various

diisocyanates, including but not limited to hexamethylene diisocyanate (HDI), methylene diisocyanate (MDI), toluene diisocyanate (TDI), and isophorone diisocyanate (IPDI) can be used. Aliphatic isocyanates are preferred. Superior color retention, adhesion, and abrasion resistance in the polyurethane top coating can be achieved in the polyurethane top coating when the crosslinking agent is a biuret or isocyanurate trimer of HDI. The biuret of HDI has the following idealized formula:



The isocyanurate trimer of HDI has the following idealized formula:



One advantage of the biurets and trimers used herein is that they result in a urethane coating that is U.V. stable per se. Thus, it is contemplated that the coatings

of the present invention can be manufactured with lower amounts of U.V. stabilizers incorporated therein, resulting in lower costs of production for the coatings.

The biurets and isocyanurate trimers of HDI utilized in the present invention preferably have a viscosity within the range of about 3 to 10,000 cps, with the preferred range being from about 50 to 5,000 cps. Low viscosity biuret and trimer crosslinking agents are preferred because they allow the total coating system to have a higher solids content and still have a viscosity that facilitates spray painting/air atomization of the coating system on the outer surface of the game ball. Biurets and trimers of HDI contemplated for use herein are sold by Bayer Corp. under the trademark DESMODUR. One such composition is DESMODUR N-3200, which is a low viscosity biuret of HDI.

The polyisocyanate or polyisocyanurate with at least two $-N=C=O$ groups equivalent weight of the biuret or trimer crosslinking agent used herein preferably is within the range of 100 to 1,200, with 150 to 300 being preferred. The biuret or trimer is preferably carried in a solvent, with the solvent solution containing from a minimum of about 40% (or less, if a quite dilute solution is preferred for some reason), alternatively about 60%, alternatively about 70%, to a maximum of 100%, alternatively about 85%, by weight of the biuret or trimer.

Suitable solvents for the polyisocyanate or polyisocyanurate with at least two $-N=C=O$ groups crosslinking agent include methyl isobutyl ketone, methyl amyl ketone, methyl isoamyl ketone, butyl acetate and propylene glycol monomethyl ether acetate, or mixtures thereof. In a particularly preferred form of the invention, the solvent is present in an amount of 15 - 70 weight % and even more preferably 40 - 70 weight % based upon the total weight of the coating system. Urethane grade solvents (i.e. low-moisture solvents) preferably are used.

It is important that the initial viscosity of the coating immediately after the parts of the coating are combined is low enough that the coating can be applied to the game

ball surface in a suitable way, such as by spraying. The coating mixture of the present invention preferably has an initial viscosity of 20 - 100 centipoise, more preferably 25 - 50 centipoise, and most preferably 30 - 40 centipoise immediately after the two parts are mixed.

In the two-part systems described above, it is preferable to include a slight excess of the polyisocyanate or polyisocyanurate with at least two $-N=C=O$ groups to insure that all of the polyol will be polymerized. If any excess polyol is present, it will not polymerize and tends to act as a plasticizer, thus resulting in a coating of decreased hardness. Preferably, the index, i.e. ratio of polyisocyanate or polyisocyanurate with at least two $-N=C=O$ groups molecules to polyol is 0.90 - 1.8, more preferably 1.0 - 1.3, and even more preferably 1.0 - 1.1. The most preferred ratio is about 1.05, as this ratio takes into account any water that may be present in the polyol, and any water vapor present in the air.

The polyol, preferably, although not necessarily, is carried in a solvent. If the material is not heated and contains no flow additives, the solvent is preferably added in an amount of about 30 - 50 wt% of the polyol. If heating and/or flow additives are used, the solvent optionally can be reduced down to 0 wt%. Generally, no more than about 70 wt% solvent is added to the polyol part of the coating. Suitable solvents for use herein include the known polyurethane solvents, for example, butyl acetate, methyl isobutyl ketone, methyl amyl ketone, methyl isoamyl ketone, propylene glycol monomethyl ether acetate, and mixtures thereof. Especially preferred as the solvent or co-solvent is methyl amyl ketone because its high dipole constant permits a greater amount of polyol or other resin solids to be dispersed therein. Surface tension modifiers also can be added. If solvent is present only in one of the two parts of the coating, it preferably is present in the polyol part.

The use of methyl amyl ketone as the solvent for the polyol component, together with a low viscosity biuret or trimer of HDI as the isocyanate component

enables a substantially higher solids content to be in the coating system than was traditionally used in game ball coating systems. Some prior known top coat coating systems typically have a solids content of 35%. The coating system of the present invention, however, preferably has a solids content of from 40 to 100%. The higher solids content results in increased transfer efficiency and decreased volatile organic carbon air emission if the coating is applied in a spray coating operation. The increased efficiency allows a reduction at least of about 5 - 10% in the amount of the coating material applied to the ball while still achieving the same coverage as prior art balls.

The functional silicone additive can be carried in either part of the mixture. The amount of functional silicone additive used depends on the final coefficient of friction of the coating that is desired. Increasing the amount of silicone additive provides for a lower coefficient of friction than that of a ball with the same coating without the silicone additive. Generally, the amount of silicone additive used will be from about 0.1 to about 5 weight % based on resin solids, preferably 1 to about 3 weight %, most preferably about 2 weight %. Examples of suitable functional silicone additives suitable for use in the invention include, but are not limited to, hydroxyl functional siloxanes such as a polyester or polyether modified hydroxyl functional polydimethylsiloxane, an acrylic functional polyester modified polydimethylsiloxane, a polyether polyester modified hydroxyl functional polydimethylsiloxane, a silicone modified polyacrylate (hydroxyl functional), and any other functional silicone additive known in the art. Functional silicone additives are available, for example, from BYK Chemie, Germany, under such trademarks as BYK® 370, BYK® 371, BYK® 373, BYK® 375, and BYK® Silclean 3700.

The catalyst conveniently can be carried in the mixture which includes the polyol. The selection of an appropriate catalyst will depend upon the polyisocyanate

or polyisocyanurate with at least two $-N=C=O$ groups which is used, and the type of polyol which is used.

The catalyst is added in an amount which far exceeds that which is recommended by polyurethane coating manufacturers. The amount of any particular catalyst to be used is that which will result in an at least 100% increase in viscosity of a volume of the coating within 30 minutes after combining the first and second parts of the coating if the volume of the coating is maintained at 25°C, 1 atm and 60% relative humidity. The catalyst typically is added in an amount of 0.01 - 10 weight % active catalyst (not including any carrier) based on total resin solids (polyol plus polyisocyanate and polyisocyanurate, excluding solvents). When the catalyst is dibutyl tin dilaurate, it preferably is added in an amount of 0.05 - 0.35 weight % active catalyst based upon total resin solids and more preferably 0.08 - 0.15 weight % based upon total resin solids. When a zirconium complex is used as the catalyst, it preferably is present in an amount of about 0.05 - 10 weight % active catalyst based upon total resin solids, and more preferably 0.1 to 2 weight % active catalyst based upon total resin solids.

Other catalysts can be used alone or in combination, preferably in amounts which produce a result that is equivalent to the result which is obtained with amounts of dibutyl tin dilaurate. Factors such as the activity of the active hydrogen atoms of the coating system, as well as catalyst cost, curing temperature and desired curing time, which may depend upon curing oven availability, may affect the decision as to what quantity of catalyst should be used. Generally, it is desirable to use a quantity of catalyst which is sufficient to achieve at least a 75% reduction in curing time, and more preferably an 85 - 95% reduction in curing time as compared to the curing time of a coating of the same thickness and having the same composition except that no catalyst is included, and which is cured under the same curing conditions.

Examples of suitable zirconium complexes suitable for use as the catalyst include, but are not limited to, K-Kat XC A209, K-Kat XC-4205 and K-Kat XC-6212, available from King Industries.

Other additives can be included in the first part of the coating system. These additives include U.V. stabilizers and absorbers, leveling agents, optical brighteners, pigments, mar and slip agents, antioxidants, and defoaming agents. These materials are added in amounts of 0 - 20 wt% of the total coating system, or more preferably 1 - 5 wt%. U.V. stabilizers function to tie up free radicals in the top coating that are produced upon exposure to ultraviolet radiation, thus maintaining the integrity of the coating. A non-limiting example of a suitable U.V. stabilizer is Tinuvin 292, a hindered amine light stabilizer sold by Ciba-Geigy Corporation, Ardsley, New York. Pigments function to increase the opacity of the coating. Preferred pigments are white pigments. Examples of white pigments suitable for use in the coating include, but are not limited to, titanium dioxide, barium, sulfate, zinc sulfide, and zinc oxide. Pigments, if used, are preferably added in amounts of 30 to 50 weight % of the total coating system.

U.V. absorbers function to absorb ultraviolet radiation and re-emit it as heat. Non-limiting examples of suitable U.V. stabilizers for use in the present invention are Tinuvin 1130, a benzotriazole U.V. absorber sold by Ciba-Geigy Corporation, and Sanduvor 3206, an oxalamide derivative sold by Sandoz Chemicals Corporation, Charlotte, North Carolina.

Suitable leveling agents which reduce the surface tension of the coating for improved coating flow include Fluorad FC-430, a fluorochemical surfactant sold by 3M Industrial Chemical Products Division, St. Paul, Minnesota, and DOW 57, a silicone additive sold by Dow Corning Corporation, Midland, Michigan.

Optical brighteners can be added to the coating system so that the coating coverage can be checked under U.V. light. Suitable optical brighteners include Uvitex

OB, 2,2'-(2,5-thiophenediyl) bis (5-ter-butylbenzoxazole), sold by Ciba-Geigy Corporation, Ardsley, New York, and Lucopure EGM, a coumarin optical brightener sold by Sandoz Chemicals Corporation, Charlotte, North Carolina.

In addition to the additives, film-forming agents and/or co-reactants can be incorporated into the polyol or polyamine portion of the coating system. Co-reactants can be, for example, compositions that further polymerize with heat. Film-forming agents include compositions that form a film after the solvent is evaporated during the polyurethane polymerization process. Such materials do not react with the polyisocyanate or polyisocyanurate portion of the coating system, but instead act independently to improve the final coating properties. A suitable polymerizing co-reactant for use herein is Cymel 303, a melamine resin sold by American Cyanamid. An example of a suitable film-forming resin is A-101, an acrylic, non-hydroxyl containing resin sold by Rohm & Haas, Philadelphia, Pennsylvania.

When the two parts of a polyurethane coating system are combined, the total system has the following general formulation:

Polyisocyanate or polyisocyanurate	
with at least two $-N=C=O$ groups	35 - 100%
Solvent	0 - 65%
Catalyst	e.g. 0.01 - 10%
Additives and/or	
co-reactants	0 - 20%.

Examples of preferred coating formulations are provided below, on Tables I and III. The coating formulation in Table III represents a low coefficient of friction (or "slick") coating formulation.

The coating system is applied to a game ball and preferably to a dimpled golf ball which is typically made of an ionomer such as Iotek (a trademark of Exxon

Chemical Co., Baytown, TX) or Surlyn (a trademark of E.I. DuPont de Nemours & Co., Wilmington, DE), natural or synthetic balata, a thermoplastic polyurethane or other non-ionomer material such as a thermoplastic or thermoset elastomer. When the cover is applied over a primer, the fully dried primer preferably, although not necessarily, consists essentially of from about 90% by weight to about 96% by weight, preferably about 90% by weight, of a water-borne dispersion of a resin selected from the group consisting of acrylic resin, polyurethane resin, and combinations thereof, and from about 4% to about 10% by weight, preferably about 5% by weight, of a polyfunctional aziridine crosslinker material. (As used here, "dispersion" includes colloidal emulsions, lattices, and other dispersed forms of the composition.)

The waterborne resin dispersion used in the primer may be an acrylic emulsion or lacquer, for example a material sold by Zeneca Resins Division of Imperial Chemical Industries, PLC, of Wilmington, Delaware under the trademark NeoCryl. Particular materials of this type include NeoCryl A-601 and NeoCryl B-723, among others.

The waterborne resin dispersion used in the primer may instead be a polyurethane prepolymer emulsion, for example a material sold by Zeneca, under the trademark NeoRez. A specific NeoRez dispersion useful herein is NeoRez R-960 emulsion. Another material which may be used is WITCOBOND W-234, supplied by Witco, Organics Division, Chicago, Illinois.

Combinations of acrylic and polyurethane dispersions are also contemplated within the scope of the present invention. The water-borne dispersions contemplated herein contain from about 5% to about 90% solids, preferably from about 20% to about 40% solids.

One of ordinary skill in the art is readily able to select a resin dispersion which is useful in a primer for the ball cover materials specified above.

The polyfunctional aziridine crosslinker materials useful herein are preferably tri- or more highly functional compounds. The preferred materials include: pentaerythritol-

tris-(β -(N-aziridiny)l propionate); trimethylol-propane-tris-(β (N-aziridiny)l)propionate); mixtures of different polyfunctional aziridines identified in U.S. Patent No. 5,057,371 (for example, from column 3, line 45 to column, line 19); the polyaziridine materials identified in U.S. Patent Nos. 5,091,239 and 4,842,950; and other polyfunctional aziridines. The patents listed in this paragraph are hereby incorporated herein by reference to exemplify polyfunctional aziridines. Representative polyfunctional aziridines which are useful herein are sold under the trade designations CX-100; XAMA-2; and XAMA-7 by the manufacturers listed in the patents previously incorporated by reference.

Other additives such as flattening agents, surfactants, flow agents, thickeners and defoamers known to those skilled in the art can be incorporated into the primer composition.

The two-part coating can be applied to the surface of a game ball by spraying, dipping, pouring, brushing, wiping or the like. Whether the coating is applied directly to a golf ball cover or over a primer coat, it is preferred that the coating is applied by spraying. When the coating is sprayed, the first and second parts of the coating are mixed and immediately sprayed onto the surface of the game ball using a spray gun. The coating is typically sprayed at an average wet thickness of no more than about 3.5 mils per coat. The two-part mixture should not be held for more than about 10 minutes and preferably no more than about 5 minutes before spraying, or it may tend to coat the inside surfaces of the spray gun. The limit as to how long it can be held will vary depending on the exact composition of coating system.

After spraying, the coated game ball is transferred to a hot, 40 - 60% relative humidity oven for curing. The required curing time-temperature combination will depend upon the composition and thickness of the coating, as well as the type and quantity of catalyst which is used. When temperatures within this range are used, curing is likely to take about one hour at 100 °F or as little as about 5 minutes at 175

°F. Particularly preferred curing times are 5 - 60 minutes or even more preferably 5 - 15 minutes, as a rapid curing time of this duration will reduce the total manufacturing time for a game ball by about 5 - 5 3/4 hours. To achieve these curing times, preferred curing temperatures range from 110 - 180°F, more preferably 150 - 170°F or even more preferably about 160°F, 40 - 60% RH. The dry coating has an average thickness of about 0.4 to 0.8 mils, and has a Sward rocker hardness (ASTM D 2134-66) of at least 10 in less than 1.5 hours, and preferably in less than 10 minutes. The fully cured coating typically has a Sward rocker hardness of 5 - 70, more preferably 5 to 40.

One of the important advantages of the quick-cure coating of the invention over prior known coatings is that the reduced curing time lends itself to use of a continuous curing process, as compared to a conventional batch type curing process. Another advantage is that the total energy use for curing a given quantity of game balls is substantially reduced. A third advantage is that because the coating system of the invention is mixed only a short period of time before it is sprayed, coating materials are conserved by mixing only the required quantity.

Having generally described the invention, the following examples are included for purposes of illustration so that the invention may be more readily understood and are in no way intended to limit the scope of the invention unless otherwise specifically indicated.

CONTROL EXAMPLE 1

Five hundred dozen control balls were made having a final top coating formed from a control coating system with a composition identical to the coating system described on Table I below with the exception that the control coating system did not contain any catalyst. To coat the controls balls, the two parts of the non-catalyst coating system were mixed in a pressure pot and were sprayed with a conventional

type of spray gun to result in a final coating having a thickness of about .6 mils. The coating was applied to primed ionomeric golf balls having a polyurethane primer coating with a thickness of about .4 mils. The primer coat was formed using a Witco waterborne polyurethane system. The golf balls were cured for 6 hours at 125°F, which are conditions appropriate for the urethane reaction to go to approximately 95% completion. After curing, the golf ball top coat had excellent adhesion and did not have an "orange peel" appearance. The control golf balls were used on a driving range for 4 months. During the 4-month period, the balls were washed occasionally, in order to maintain their white appearance. After use, the balls were tested for adhesion and abrasion resistance, and were found to have no lifting or cracking of the top coating in dimples or on lands.

EXAMPLE 1

A two-part polyurethane coating system having the composition shown on Table 1 was prepared, with the polyol part and isocyanate biuret part being kept in separate vessels. The first and second parts were mixed and were then immediately sprayed on the outer surface of two hundred dozen primed golf balls that were identical to the primed, unfinished gold balls used in Control Example 1. The polyol and isocyanate parts were mixed in a ratio of 2 parts by weight of polyol part per 1 part by weight of the isocyanate part. The apparatus used for spraying was a commercially available two-compound spraying apparatus, which was revised and adapted to reduce spraying volume and increase spraying frequency. The balls were cured for 30 minutes at 130°F. After curing, the balls were dry to the touch and had a final top coating of about 0.6 mils, over a primer coating with a thickness of about 0.4 mils. The balls were examined and were found to have excellent adhesion of the top coat. The adhesion was comparable to that of the control sample. Furthermore, the golf balls did not have an "orange peel" appearance.

One dozen of the golf balls were placed in a weatherometer with a XENON lamp which was operated for 48 hours using cycle 5 at 0.65W/m^2 . This set of one dozen golf balls, along with five dozen of the coated golf balls which had not been placed in the weatherometer, were subjected to a wet barrel test which involved soaking the golf balls in water for at least three hours, and then firing each ball 100 times at a velocity of 135 ft/sec at 72°F into a five-sided container, the walls of which are steel plates that have grooves milled therein to simulate the grooves present on a golf club face. The results of weatherometer and barrel testing were the same for the golf balls of Example 1 as for the control golf balls.

The golf balls which were not subjected to the weatherometer and wet barrel testing were used on the same driving range for four months. During the 4-month period, the balls were washed at the same frequency as the control balls. After the 4-month testing period, the golf balls of Example 1 were tested for adhesion and abrasion resistance and were found to have no lifting or cracking of the top coating, in dimples or on lands, and thus had properties of adhesion and abrasion resistance comparable to that of the control balls.

EXAMPLE 2

The coating formulation of Table I was prepared in two separate parts with the exception that no catalyst was added. The polyol mixture was separated into six separate batches. Dibutyl tin dilaurate catalyst (Dabco T-12, Air Products and Chemicals, Inc., Allentown, PA) which contains 97 weight % dibutyl tin dilaurate and 3 weight % lauric acid was added to the polyol part of each batch in a different amount as is shown on Table II below. Catalyst amounts are percent by weight based upon 100 parts by weight of polyol. The sixth batch was the control, and no catalyst was added. Each polyol mixture was combined with a quantity of isocyanate part which corresponds to Table I at 25°C , 1 atm and about 60% relative humidity, and the resulting mixture was placed in a cylindrical container such that the volume of the liquid was that of a cylinder 8 cm high with a diameter of 9.5 cm (180.5 cm^3). The

viscosity of each of the six coating mixtures was measured at five minute intervals from 0 to 45 minutes. The resulting values of viscosity are shown on Table II.

As shown in Table II, the viscosity of the coating mixture changed very rapidly when high concentrations of catalyst were used.

As will be apparent to persons skilled in the art, various modifications and adaptations of the above described invention will become readily apparent without departing from the spirit and scope of the invention.

Table I

	phr	%COMPLETE	%PART	wt/gal	Solids	Solids %	MIXTURE	OH EQ %	OH PHR
PART I									
1. Saturated polyester polyol ¹	100	29.81%	43.75%	9.2	65.00%	19.376%	OH EQ 330	253.846	100.000
2. Linear saturated polyester polyol ²	30	8.94%	13.13%	9.2	80.00%	7.154%	500	115.385	30.000
3. Solvent 1 ³	10	2.98%	4.38%	6.67	0.00%	0.000%			
4. Solvent 2 ⁴	35	10.43%	15.31%	7.35	0.00%	0.000%	0	0.000	0.000
5. Solvent 3 ⁵	50	14.90%	21.88%	6.8	0.00%	0.000%			
6. Flow additive ⁶	0.3	0.09%	0.13%	9.16	100.00%	0.089%			
7. UV absorber (narrow) ⁷	2	0.60%	0.88%	8.41	100.00%	0.596%			
8. UV stabilizer ⁸	1	0.30%	0.44%	8.267	100.00%	0.298%			
9. Optical brightener ⁹	0.1	0.03%	0.04%	10.579	100.00%	0.030%			
10. Catalyst ¹⁰	0.15	0.04%	0.07%	8.747	100.00%	0.045%			
Subtotal	228.55	68.130%	100.00%			27.589%	830	369.231	130.000
PART II									
11. Isocyanate biuret	66.91	19.95%	62.59%	9.3	100.00%	19.947%	NCO EQ 181	181.000	66.913
12. Solvent 1 ³	40	11.92%	37.41	6.67	0.00%	0.000%			
Subtotal	106.91	31.870%	100.00%			19.947%		181.000	
Total	335.46	100.00%				47.535%			

¹ Desmophen 651A-65 (Bayer Corp.)	⁴ Butyl Acetate (Sandoz Chem. Corp.)	⁷ Sanduvor 3206 (Air Prod. Allentown, PA)	¹⁰ DABCO T-12 (Air Prod. Allentown, PA)		
² Desmophen 67080 (Bayer Corp.)	⁵ Methyl Amyl Ketone (Ciba Geigy Chem. Co.)	⁸ Tinuvin 292 (Bayer Corp.)	¹¹ Desmodur N-3200 (Bayer Corp.)	Solids	47.535%
³ Methyl Isobutyl Ketone	⁶ 3M FC 430 (3M Corp.)	⁹ Uvitex OB (Ciba Geigy Chem. Co.)		Index	1.02
					MIX RATIO
					0.468
					140.337

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Table II

Minutes		Viscosity (cps)					
	Cat. Conc.	0.2%	0.15%	0.1%	0.05%	0.01%	Control (no cat)
0		35	35	35	35	35	35
5		40	40	35	35	35	35
10		48	45	40	35	35	35
15		75	55	40	40	40	40
20		245	85	50	40	40	40
25		solid	210	60	45	45	40
30		solid	solid	90	50	45	40
35		solid	solid	160	60	45	40
40		solid	solid	660	70	50	40
45		solid	solid	solid	85	55	40

Table III

Part I	
Component	Amount (lbs.)
Polyol portion	644.0
Wax dispersion	9.77
Functional silicone (Byk® 370)	9.77
Teflon® dispersion	3.26
Antistatic agent	2.50
Subtotal	669.3 lbs.
Part II	
Isocyanate portion	350.52
Total	1019.82 lbs.

Note: Mix ratio of Part I to Part II is 2:1 (by volume)

IN THE CLAIMS:

1. A game ball coating system comprising:

a polyol,

at least one of a polyisocyanate containing at least two $-N=C=O$ groups and a polyisocyanurate containing at least two $-N=C=O$ groups which is present in a quantity appropriate to provide an equivalent weight ratio of $-N=C=O$ to $-OH$ in the range of 0.90 to 1.8,

15 to 70 wt % of a solvent based upon the weight of the coating system, and

a compatible catalyst, the catalyst being present in a quantity sufficient to cure a 3.5 mil thick layer of the coating composition to a Sward rocker hardness of at least 10 in less than 10 minutes if the later is cured at a temperature of about 100 to 180° F, the coating system providing a fully cured coating with a Sward rocker hardness of 10 to 70.

2. A game ball coating system according to claim 1, wherein the coating system includes a first part comprising the polyol, at least a portion of the solvent, and the catalyst, and a second part comprising the polyisocyanate.

3. A game ball coating system according to claim 1, wherein the catalyst is present in the coating system in a quantity sufficient to provide for an at least 100% increase in viscosity within 30 minutes if the coating were maintained at 25°C, 1 atm and 60% relative humidity.

4. A game ball coating system according to claim 1, wherein the fully cured coating has a Sward rocker hardness of 10 to 40.

5. A game ball coating system according to claim 1, further comprising a functional silicone additive.

6. A game ball coating system according to claim 1, wherein the polyisocyanate includes at least one member selected from the group consisting of biurets and isocyanurate trimers of hexamethylene diisocyanate.

7. A game ball coating system according to claim 5, wherein the polyisocyanate includes at least one member selected from the group consisting of biurets and isocyanurate trimers of hexamethylene diisocyanate.

8. A game ball coating system according to claim 1, wherein the catalyst comprises at least one member selected from the group consisting of zirconium complex, dibutyl tin dilaurate, dibutyl acetylacetonate, dibutyl tin dibutoxide, dibutyl tin sulphide, dibutyl tin di-2-ethylhexanoate, dibutyl tin (IV) diacetate, dialkyltin (IV) oxide, tributyl tin lauryl mercaptate, dibutyl tin dichloride, tetrabutyl titanate, tertiary amines, mercaptides, stannous octoate, potassium octoate, zinc octoate, diaza compounds, and potassium acetate.

9. A game ball coating system according to claim 1, wherein the catalyst is at least one member selected from the group consisting of zirconium complex, dialkyl tin catalysts, mercaptide catalysts, and metal octoate catalysts.

10. A game ball coating system according to claim 1, wherein the catalyst is a zirconium complex.

11. A game ball coating system according to claim 1, wherein the solvent includes at least one member selected from the group consisting of ketones, esters and acetates.

12. A game ball coating system according to claim 1, wherein the coating system contains at least 0.1 wt % zirconium complex active catalyst based upon total resin solids.

13. A game ball coating system according to claim 1, wherein the coating system contains 40 - 70 wt % solvent based upon the total weight of the coating mixture.

14. A game ball coating system according to claim 5, wherein the functional silicone additive is present in an amount of from about 0.1 to 5 weight % based on total resin solids.

15. A game ball coating system according to claim 1, wherein the coating system contains methyl amyl ketone.

16. A game ball coating system according to claim 15, wherein the coating mixture further contains at least one of methyl isoamyl ketone, methyl isobutyl ketone and butyl acetate as a solvent.

17. A game ball coating system according to claim 1, wherein the coating system is a golf ball coating system.

18. A game ball coating system according to claim 1, further comprising a white pigment.

19. A game ball coating system comprising:

a polyol,

at least one of a polyisocyanate containing at least two $-N=C=O$ groups and a polyisocyanurate containing at least two $-N=C=O$ groups which is present in a

quantity appropriate to provide an equivalent weight ratio of $-N=C=O$ to $-OH$ in the range of 0.90 to 1.8,

a functional silicone additive,

15 to 70 wt % of a solvent based upon the weight of the coating system, and

a compatible catalyst, the catalyst being present in a quantity sufficient to cure a 3.5 mil thick layer of the coating composition to a Sward rocker hardness of at least 10 in less than 10 minutes if the later is cured at a temperature of about 100 to 180° F, the coating system providing a fully cured coating with a Sward rocker hardness of 10 to 70.

20. A golf ball coating system comprising:

a polyol,

at least one of a polyisocyanate containing at least two $-N=C=O$ groups and a polyisocyanurate containing at least two $-N=C=O$ groups which is present in a quantity appropriate to provide an equivalent weight ratio of $-N=C=O$ to $-OH$ in the range of 0.90 to 1.8,

a functional silicone additive,

15 to 70 wt % of a solvent based upon the weight of the coating system, and

a zirconium complex catalyst, the catalyst being present in a quantity sufficient to cure a 3.5 mil thick layer of the coating composition to a Sward rocker hardness of at least 10 in less than 10 minutes if the later is cured at a temperature of about 100 to 180° F, the coating system providing a fully cured coating with a Sward rocker hardness of 10 to 70.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/16566

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08G 18/42, 18/22, 18/24; A63B 37/12

US CL : 473/378, 600, 607; 524/261, 265, 267, 730; 528/28, 48, 49, 52, 53, 55, 56, 57, 58, 67, 73, 75, 80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 473/378, 600, 607; 524/261, 265, 267, 730; 528/28, 48, 49, 52, 53, 55, 56, 57, 58, 67, 73, 75, 80

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,607,062 A (MEGNA) 19 August 1986 (19.08.1986), column 6, lines 3, 4, and 9-12, column 8, lines 26-29 and 34.	1-4,6,8,9,11,13,15-18
Y	US 5,091,265 A (KENNEDY et al.) 25 February 1992 (25.02.1992), abstract, column 4, lines 32-68, column 6, lines 27-68, column 7, lines 62-66.	1-20
Y	US 5,502,100 A (MARUOKA et al.) 26 March 1996 (26.03.1996), column 1, lines 54-61, column 2, line 6.	1-20
Y	US 5,846,897 A (BLANK et al.) 08 December 1998 (08.12.1998), column 5, lines 41-63.	1-20
Y	US 5,965,686 A (BLANK et al.) 12 October 1999 (12.10.1999), column 6, lines 12-36.	1-20
A	US 6,340,503 B1 (SIMONDS et al.) 22 January 2002 (22.01.2002).	1-20
Y	US 6,395,861 B1 (KENNEDY, III) 28 May 2002 (28.05.2002), abstract, columns 2-6.	1-20
P, Y	US 6,398,669 B1 (YOKOTA et al.) 04 June 2002 (04.06.2002), abstract.	1-20
Y	Oertel. Polyurethane Handbook: Chemistry - Raw Materials - Processing - Applications - Properties. Hanser Publishers. New York. 1985. pages 515, 525, 526.	1-4,6,8,9,11,13,15-18



Further documents are listed in the continuation of Box C.



See patent family annex.

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document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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25 September 2003 (25.09.2003)

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