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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C08F 8/30

A1

(11) International Publication Number: **WO 92/19656**

(43) International Publication Date: 12 November 1992 (12.11.92)

(21) International Application Number: PCT/US92/03402

(22) International Filing Date: 24 April 1992 (24.04.92)

(30) Priority data:
691,552 25 April 1991 (25.04.91) US

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(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), LU (European patent), MC (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: COATING COMPOSITION AND METHOD

(57) Abstract

Improved coatings particularly useful for golf balls are based on modified acrylic urethanes. The coatings have high film clarity, gloss, durability, flexibility and resistance to weathering and abrasion. The coating composition is applied, typically by spraying and preferably after application of a suitable primer. The coating composition is a mixture of a hard acrylic polymer having a functionality reactive with an isocyanate and isocyanate-reactive modifiers, reacted together in a solvent with an isocyanate such as polyisocyanate. Golf balls with these coatings exhibit improved hardness and flexibility.

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COATING COMPOSITION AND METHOD

DESCRIPTION

Related U.S. Application Data

This is a continuation-in-part of co-pending U.S. application Ser. No. 07/691,552, filed April 25, 1991.

Technical Field

The invention relates to improved coatings, more particularly to coatings especially useful for golf balls due to their superior properties uniquely adapted for this use.

Golf balls must be durable and have an attractive appearance throughout their lives, which are now extended due to the high durability of new materials of construction.

The advent of cut resistant golf balls, particularly those having covers made of high impact natural or synthetic polymeric materials such as those ionomer resins sold under the trademark Surlyn®, has increased the need for durable coatings to improve the appearance of the balls. Conventionally, these balls are provided with a primer coat, e.g. an organic-solvent based epoxy or a water-based polymer, and are then over coated with a polyurethane which provides desirable properties in terms of flexibility, but achieves some desirable properties only at the expense of others.

There is a present need for an improved coating composition which is capable of providing high film clarity, gloss, durability, flexibility and resistance to weathering and abrasion.

Disclosure of Invention

It is an object of the invention to provide a coating composition especially adapted for uses which require impact durability and flexibility.

It is another object of the invention to provide a coating composition which provides high clarity and high gloss and also has good resistance to weathering and abrasion.

It is a more specific object of the invention to provide a coating composition having all of the above properties for sporting goods, such as golf balls.

These and other objects are achieved by the present invention which provides an improved coating composition, an improved coating method, and improved coatings and articles employing them.

The coating composition of the invention comprises: (a) a hard acrylic polymer having a functionality reactive with an isocyanate; (b) an isocyanate; (c) a solvent for application flow and leveling; and (d) a modifying resin which is also isocyanate reactive but imparts flexibility and/or abrasion resistance to the final coating. In preferred embodiments, the acrylic polymer, the isocyanate, and the isocyanate-reactive modifiere each have equivalent weights of at least about 200.

The method of the invention comprises: (a) optionally applying a primer layer to a substrate, such as natural or synthetic polymer resins such as ionomeric polymers; (b) spraying onto the surface a coating composition as defined above, and (c) drying and curing the coating.

The coated article comprises: a substrate, such as a golf ball having a primed ionomeric layer overcoated with a dried, cured layer of an acrylic urethane coating.

Best Mode For Carrying Out the Invention

The invention will be described below in greater detail with specific reference to the use of golf ball coatings. Other uses, e.g. bowling pins, are intended, but are not detailed for the sake of conciseness.

The invention, in one of its preferred aspects, provides a modified acrylic urethane coating system for Surlyn® covered golf balls. The coating system comprises an acrylic resin having a functionality reactive with a polyisocyanate. The functionality can be a member selected from the group consisting of hydroxyl, amine, amide, carboxyl and mixtures of any of these. The acrylic typically has a functional group (e.g., hydroxyl) equivalent weight on a solid resin basis of from 200 to 2000, preferably from 500 to 700. The modifiers function similarly to plasticizers and/or surface hardeners but are reactive with the isocyanate. The polyisocyanate can be a suitable prepolymer, homopolymer or copolymer of diisocyanates such as toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI). The products, e.g. ionomer-golf balls, will exhibit good hardness, flexibility, weather resistance, brightness, abrasion resistance and clarity.

Good golf ball cover materials have a balance of forming and final properties including good flowability, good mold release, moderate stiffness, high abrasion resistance, high tear strength, high resilience, and the like. Preferred polymeric materials are ionomer resins comprising copolymers of ethylene and unsaturated monocarboxylic acids which are available under the trademark Surlyn® from E.I. DuPont de Nemours Company of Wilmington, Delaware. These ionic copolymers are sodium, lithium, or zinc salts of reaction products of olefins having from 2 to 8 carbon atoms and unsaturated monocarboxylic acids having from 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized.

The use of a single ionic copolymer as golf ball cover stock is described in U.S. Patent No. 3,454,280 issued July 8, 1969. The use of mixed Surlyn® resins is described in U.S. Patent No. 3,819,768 issued June 25, 1974. Other ionic copolymers are described in U.S. Patent No. 3,264,272 issued August 2, 1966.

In addition to the above-described preferred Surlyn® resins, other thermoplastic materials and thermosetting materials including natural and synthetic polymeric materials can be employed. Balata and gutta percha, previously available as natural materials are now available as synthetic polymeric materials and are suitable for use in accordance with this invention. Other materials include urethane as well as other synthetic polymers. The golf ball comprises a highly resilient core having a cover stock of one of these high impact materials, or mixtures thereof.

To prepare the elastomeric, e.g. ionomer, or other substrate for coating with the composition of this invention, a primer effective to promote bonding between the coating and the substrate is preferably employed. Among the effective primers are solvent-based or water-based epoxies and water-based acrylic or urethane polymers. Exemplary of the epoxy primers is a two component solvent-based epoxy, available as TCL-3707/3631 from Technical Coatings Laboratory, Inc, Avon, Connecticut. Exemplary of the water-based primers is a modified acrylic polymer coating available as TCL-5500 from the same source as above. Other primers, available from other suppliers are also effective. Primers are not always required, but do enhance results for most users.

The primer is applied according to specifications for the particular material, e.g. spraying to a thickness of about 1/8 to 1/2 mil. Epoxy primers of the type identified above are typically cured for from 10 minutes to 24 hours, at from room temperature to 150°F. The epoxy coating has to be essentially solvent free before top coating. The water-based polymers are typically cured for from 1 to 45 minutes at from room temperature to 150°F.

Following priming, the coating composition of the invention is applied. The coating composition itself comprises an acrylic resin having an isocyanate reactive functionality, an isocyanate, a solvent, and a isocyanate-reactive modifier. It can also have, as desired, various catalysts, promoters, driers, hardeners, brighteners and the like.

The acrylic resin can be a homo or copolymer of acrylic monomers having the isocyanate-reactive functionalities, e.g. selected from the group consisting of hydroxyl, amine, amide, carboxyl, and mixtures of any of these. One embodiment employs predominantly hydroxyl group isocyanate reactive functionalities. The monomers can be any of those effective for producing the desired acrylic resins, and can, for example, be selected from the group consisting of acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, acrylonitrile, acrylamide, and the like monomers and mixtures of these. Preferred blends comprise any of the above and the like, and preferred embodiments are hard polymers having a minimum of 10% styrene in the monomer composition. Some embodiments have at least about 20% styrene. Some coatings of this invention contain acrylic polymers having less than about 1% of alpha-beta ethylenically unsaturated carboxylic acid monomers.

The acrylic resins will be prepared in conventional fashion to have isocyanate-functional equivalent weights typically above 200 and below 2000. Typically this involves solution vinyl polymerization where the monomers are added to a catalyst-containing solvent gradually over the course of the reaction and in amounts effective to give the desired equivalent weight. Preferred equivalent weights will be in the range of from 400 to about 600 on a resin solid basis. One preferred acrylic resin is based on methyl methacrylate and hydroxypropyl methacrylate monomers and has an equivalent weight of between 500 and 600, on a solids basis. Typical available resins of this type are Rohm and Haas's AU 608, AT-400, AT-410 and Henkel's G-Cure 867 and 868. It is preferable to mix the reactive isocyanate in a two component system just prior to application. A blend of solvents is employed to achieve a suitable solids concentration and viscosity for good mixing, application and reaction. One material of this type is TCL-5823, available from Technical Coatings Laboratory, Inc.

The isocyanate component of the coating system can be any suitable isocyanate, including prepolymers, homopolymers or copolymers of diisocyanates such as toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and the like. The various families of isocyanates that have been investigated have been hexamethylene diisocyanate biuret, hexamethylene/toluene diisocyanate copolymers, toluene diisocyante bicyanurate trimer, toluene diisocyante/trimethyol propane adduct, isophorone diisocyanate (IPDI) based prepolymer toluene diisocyanate multi-functional prepolymer, and hexamethylene diisocyanate trimer.

The isocyanates are prepared in known manner and typically have equivalent weights to the hydroxyl or other acrylic isocyanate reactive group of at least about 100, and preferably from 200 to 800, e.g. 300 to 500 on a solids basis. The isocyanates are preferably employed as prepolymer solutions with suitable solids, concentrations and viscosities for effective mixing application, drying and curing.

A one package polyurethane system may also be used. This system uses a blocked isocyanate such as Miles's Desmodur™ BL-1185. Limitations of use may be related to the thermo-plastic characteristics of the substrate.

The modifiers are typically added to the final reaction mixture as a preblend with the acrylic resin. The modifiers employed in the coating composition will be those which are effective to impart flexibility and abrasion resistance to the final coating. Organic plasticizers can also be used in this acrylic coating composition. Monomeric and polymeric plasticizers allow the coating to increase its workability and its flexibility. Phthalic anhydride esters such as dioctyl phthalate, dibutyl phthalate and dicyclohexyl phthalate may be used. Epoxidized soya oils, oil free and oil modified alkyds can also be incorporated. Alkylene glycol esters of benzoic and adipate acid such as ethylene glycol adipate benzoate, neopentyl adipate benzoate and ethylene glycol adipate benzoate phthalate can also be used in the coating compostion. The preferred modifier is sufficiently reactive to prevent migration to the surface of the coating. The modifiers preferably have isocyanate reactive functional groups at an equivalent weight effective for this purpose, e.g. under 10,000 and preferably from 200 to 2000 on a solids basis.

Among the suitable modifiers are the members selected from the group consisting of cellulosic esters; silicones; silanes; caprolactones; vinyl polymers; acrylic polymers with carboxyl, amino or hydroxyl functionality such as Henkel's G-Cure® 105P70 and G-Cure® 806; polyesters; polyester-modified, hydroxylfunctional polydimethylsiloxane; and mixtures of these. Preferred among these are caprolactones, such as Tone® polyols, available from Union Carbide Corporation, Danbury, Connecticut and characterized by a hydroxyl equivalent weight of about 1000. Some more specific examples of suitable modifiers include the following: caprolactone polyols di and trifunctional, with equivalent weights 200 to 1800, preferably 800 to 1200; polyesters having equivalent weights of 300 to 1500; cellulosic modifiers including cellulose acetate butyrate or cellulose acetate proprionate; and solution vinyls, including the medium to low viscosity types.

The solvents employed for the acrylic and the isocyanate components will be chosen for their primary role as well as their compatibility with the overall composition, the mixing of the various components, the compatibility with the intended substrate and the ease of application, drying and curing of the coating composition. Among the solvents are n-butyl acetate, xylene, toluene, propylene, glycol monomethyl ether acetate, ethyl acetate, Cellosolve® acetate, and the like. All solvents are essentially water-free, i.e., urethane grade.

Isocyanates are the crosslinkers used in the acrylic urethane coating. These are polymeric in nature, when mixed stoichiometrically with the acrylic urethane polyol produces a tough flexible coating. The mix ratio for the polyol-isocyanate combination are measured as the amount of NCO isocyanate needed to react with an equivalent amount of hydroxyl groups. Stoichiometrically the amount of NCO/OH ratio needed would be 1.0/1.0; however excess isocyanate is generally used since the isocyanate is moisture sensitive and its effectiveness would diminish upon exposure to air. The range of NCO/OH can be from 1.0/1 up to 1.8/1. Changing the mix ratios will effect the physical properties of the coating; hardness, durability and pot life are very common variables when this ratio is changed. The preferred range for the NCO/OH is about 1.1/1 to 1.5/1.

In addition to the above, the coating composition can include other additives in amounts effective for their intended purposes. For example, catalysts such as dibutyltin dilaurate, metal driers, or tertiary amines can be employed at effective levels, e.g., of 0.01 to 0.05% based on vehicle solids. The type and level may be adjusted as needed to achieve desired pot life and cure times. Also, various color additives such as titanium dioxide, driers such as cobalt salts, managanese salts or calcium salts, and optical brighteners and ultraviolet absorbers such as Ciba-Geigy Uvitex OB®, Tinuvin® 328 and Tinuvin® 770, or equivalents, can be employed in amounts desired.

The coating composition is formed for application by blending an acrylic resin solution and an isocyanate solution prior to application. The proportions of isocyanate and acrylic resins will be as noted above. The acrylic resin premix will typically contain: from 50% to 100%, e.g. from 60 to 98% acrylic resin solids, up to 50% modifier solids; e.g. 2 to 40%; and from 20 to 90% solvent based on the weight of the solids. Similarly, an isocyanate premix is formed containing from 20 to 80, preferably from 68 to 72% isocyanate solids and from 20 to 80, preferably from 32 to 38%. These amounts can be varied widely as processing needs and capabilities dictate.

Various spray techniques can be used to apply these coatings. These include, but are not necessarily limited to, air atomized with pressure or suction feed with or without heat, airless, airless hot spray and electrostatic. For the purposes of this invention, a Binks No. 18 suction spray gun equipped with a 62 fluid nozzle, a 62 fluid cap and a 66 PG air cap can very effectively be used. The application technique should ensure a uniform coating on the ball or other substitutes. In a production application, two to four fixed guns may be required to give a uniform coating. The coating is applied in any desired thickness, typically to give a final thickness of from 1/2 to 1 mil.

The applied urethane coating will cure as typical urethanes. The rate of cure will depend upon temperature and humidity. The preferred curing cycle is 24 hours at 105°F and 50% relative humidity. Faster cures can be achieved by increasing the cure temperature. For example, the balls can cure in 2 hours at 140°F and 50% relative humidity. Various catalysts or catalyst combinations can be used to help accelerate the cure.

The following examples are presented to further illustrate and explain the invention and are not to be taken as limiting in any respect. Unless otherwise indicated, all parts and percentages are based on the weight of the particular composition or component at the indicated stage of processing.

Example 1

This example describes the preparation of a coating composition according to the invention, and the application of that composition to a Surlyn® ionomer covered golf ball to produce an improved golf ball of the invention. An acrylic premix is prepared by blending an acrylic resin prepared from

2-hydroxyethyl acrylate, having a hydroxyl equivalent weight of 600 (solids basis), with the following other components in the indicated amounts.

Acrylic Resin Premix

Component	Parts
Acrylic resin (solids)	36.5
Caprolactone	2.5
VAGD® vinyl solution (20% solids) (ethyl acetate solvent, from Union Carbide)	12.0
Cellulosic solution (20% solids) (cellulose acetate butyrate polymer in ethyl acetate solvent)	2.5
Solvents (ethyl acetate and toluene, 1:1)	46.4
Miscellaneous additives (catalyst and optical brightener)	0.1
	100.0

Separately, an isocyanate premix is prepared from a hexamethylene diisocyanate biuret prepolymer having an equivalent weight of about 190, based on solids, by mixing the following components in the amounts indicated.

Isocyanate Premix

Component	Parts
Isocyanate prepolymer (solids)	30
Solvents (Xylene and n-butyl acetate)	70
	100

A sprayable coating composition is then prepared by mixing 100 parts of the acrylic resin premix with 51 parts by weight of the isocyanate premix.

A Surlyn® ionomer covered golf ball is prepared for coating with the above coating composition by first priming the surface by spray coating with a solution of a commercial solvent-based epoxy primer (TCL-3707/3631) to provide a primer coating thickness of 1/8 to 1/4 mil. The primer coating is dried for 45 minutes at 145°F.

The sprayable coating composition is then applied by spraying by means of a Binks no. 18 suction spray gun equipped with a 62 fluid nozzle, a 62 fluid cap, and a 66 PG air cap. The coating is sufficient to provide a film thickness of 1/2 to 3/4 mil. The coating is flashed at 75°F for 20 minutes and then cured for 24 hours at 145°F.

Example 2

The procedure of Example 1 is repeated but this time the premixes and their proportions meet the following criteria:

Acrylic Resin Premix

Component	Parts
Acrylic resin (solids)	18.0
Solvent	44.5
Polyester	6.0
Vinyl solution (20% solids)	28.3
Cellulosic solution (20% solids)	2.5
Miscellaneous additives	0.7
	100.0

Isocyanate Premix

Component	Parts
Isocyanate prepolymer (HDI/HDI - TDI copolymer/ TDI-trimethyolpropane)	31.6%
Solvents (n-butyl acetate, xylene)	68.4%
	100.0

The ratio of acrylic resin premix to isocyanate premix for preparing a coating composition is 100:37.5.

Example 3

The procedure for Example 2 is again repeated but this time the premix isocyanate and the proportions of the two premixes are modified as follows:

Isocyanate Premix

Component	Parts
Isocyanate (solids) (HDI biuret/HDI-TDI copolymer/ TDI Bicyanurate copolymer)	31.6
Solvent	68.4
	100.0

The ratio of acrylic resin premix to isocyanate premix for preparing a composition was 100:38. To these, two components are added 73.0 parts of a blended thinner comprising aromatic hydrocarbons and esters. Flash conditions are modified to account for the high level of solvent in the coating composition.

Example 4

Acrylic Resin Premix

Component	Parts
Acrylic resin solution (60% solids)	36.5
Caprolactone	7.5
Vinyl solution (20% solids)	10.1
Solvent	45.0
Miscellaneous additives	0.9
	100.0

Isocyanate Premix

Component	Parts
Isocyanate prepolymer (solids) (50-50 HDI/TDI-HDI)	32.0
Solvent (ethyl acetate, butyl acetate, toluene)	68.0
	100.0

The two premixes are mixed at a ratio of acrylic resin premix to isocyanate premix of 100:36.5.

Example 5

The procedure of Example 1 is again repeated but this time the premix isocyanate and the proportions of the two premixes are modified as follows:

Acrylic Resin Premix

Component	Parts
Acrylic resin (solids)	30.0
Vinyl solution (20% solids)	10.8
Solvent	57.3
Miscellaneous additives	1.9
	100.0

Isocyanate Premix

Component	Parts
Isocyanate (solids) (TDI prepolymer)	42.0
Solvent	58.0
	100.0

The ratio of acrylic resin premix to isocyanate premix for preparing a composition was 100:36.5.

Example 6

The procedure of Example 5 is again repeated but this time the premix isocyanate is modified as follows:

Isocyanate Premix

Component	Parts
Isocyanate (solids) (IPDI prepolymer)	59.8
Solvent	40.2
	100.0

The two premix solutions are mixed at a ratio of acrylic resin solution to isocyanate solution of 100:36.5.

Example 7

The procedure of Example 1 is again repeated but this time the isocyanate premix and the proportions of the two premixes are modified as follows:

Acrylic Resin Premix

Component	Parts
Acrylic (solids)	21.9
Caprolactone (solids)	1.6
Vinyl solution (20% solids)	12.0
Solvent	63.2
Silicone (solids)	1.0
Miscellaneous additives	0.3
	100.0

Isocyanate Premix

Component	Parts
Isocyanate (solids) (HDI/TDI-HDI copolymer)	46.0
Solvent	54.0
	100.0

The ratio of acrylic resin premix to isocyanate premix for preparing a composition was 100:40.3.

Example 8

The procedure for Example 1 is again repeated but this time the premix isocyanate and the proportions of the two premixes are modified as follows:

Acrylic Resin Premix

Component	Parts
Acrylic (solids)	36.5
Caprolactone (solids)	7.5
Vinyl solution (20% solids)	10.0
Solvent	45.1
Miscellaneous additives	0.9
	100.0

Isocyanate Premix

Component	Parts
Isocyanate (solids)	
HDI prepolymer	18.4
TDI prepolymer	27.6
Solvent	54.0
	100.0

The ratio of acrylic resin premix to isocyanate premix for preparing a composition was 100:38.2.

Example 9

The procedure for Example 8 is again repeated but this time the premix isocyanate and the proportions of the two premixes are modified as follows:

Isocyanate Premix

Component	Parts
Isocyanate (solids)	
HDI prepolymer	13.8
TDI prepolymer	32.2
Solvent	54
	100.0

The ratio of acrylic resin premix to isocyanate premix for preparing a composition was 100:40.

Example 10

The procedure for Example 8 is again repeated but this time the premix isocyanate and the proportions of the two premixes are modified as follows:

Isocyanate Premix

Component	Parts
Isocyanate (solids)	
HDI prepolymer	11.5
TDI prepolymer	34.5
Solvent	54.0
	100.0

The ratio of acrylic resin premix to isocyanate premix for preparing a composition was 100:41.

The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within the scope of the invention which is defined by the following claims.

Claims

1. A coating composition comprising

(a) a hard acrylic polymer having a functionality reactive with an isocyanate and an equivalent weight of at least about 200;

(b) an isocyanate having an equivalent weight of at least about 200;

(c) an isocyanate-reactive modifier having an equivalent weight of at least about 200 effective to improve flexibility while retaining good abrasion resistance; and

(d) a solvent.

2. A composition according to claim 1 wherein the acrylic polymer has an equivalent weight of between about 200 and about 2000, the isocyanate has an equivalent weight of between about 200 and about 2000, and the isocyanate-reactive modifier has an equivalent weight of between about 200 and about 2000.

3. A composition according to claim 2 wherein the acrylic polymer has an equivalent weight of between about 500 and about 700, the isocyanate has an equivalent weight of between about 300 and about 500, and the isocyanate-reactive modifier has an equivalent weight of between about 300 and about 1500.

4. A composition according to any of claims 1 to 3 wherein the acrylic polymer comprises monomers selected from the group consisting of styrene, methyl methacrylate, hydroxypropyl methacrylate monomers, and mixtures of these, and has a styrene content of at least about 10%.

5. A composition according to any of claims 1 to 4 wherein the functionality reactive with an isocyanate in the acrylic polymer is selected from the group consisting of hydroxyl,

carboxyl, amine, amide, and mixtures of these, the isocyanate is a polyisocyanate comprising a prepolymer, homopolymer, copolymer or biuret comprising residues of at least one of toluene diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate, and the isocyanate-reactive modifier is selected from the group consisting of cellulosic esters, silicones, silanes, caprolactones, vinyl polymers, acrylic polymers, polyesters, and polyester-modified hydroxy functional polydimethylsiloxanes.

6. A composition according to any of claims 1 to 5 wherein the functionality reactive with isocyanate on the acrylic polymer is an hydroxyl group, and the ratio of the isocyanate equivalent weight to the hydroxyl equivalent weight in the coating varies between about 1 to 1 to about 1.5 to 1.

7. A composition according to any of claims 1 to 6 wherein the acrylic polymer contains less than about 1% of an alpha-beta ethylenically unsaturated carboxylic acid monomer.

8. A method for enhacing the surface characteristics of a substrate comprising applying to the surface of the substrate a coating composition as set forth in any of claims 1 to 7, and drying and curing the coating composition.

9. A method for enhancing the surface characteristics of a substrate comprising first mixing the acrylic polymer, the isocyanate-reactive modifier, and the solvent of any of claims 1 to 7, and then adding the isocyanate of any of claims 1 to 7 before applying the composition to the surface of the substrate.

10. A method according to claims 8 or 9 wherein the substrate is a golf ball having a cover stock of ionomeric material.

11. A golf ball made according to the method of claim 10.

12. A method according to claim 10 wherein a primer is applied to the ionomeric golf ball cover stock prior to applying the coating composition.

13. A golf ball comprising

(a) a highly resilient core having a cover stock of high impact material; and

(b) a coating on said cover stock comprising an acrylic polymer having a functionality reactive with an isocyanate and an equivalent weight of at least about 200; an isocyanate having an equivalent weight of at least about 200; an isocyanate-reactive modifier having an equivalent weight of at least about 200 effective to improve flexibility while retaining good abrasion resistance; and a solvent.

14. A golf ball according to claim 13 further comprising a primer layer between said cover stock and said coating.

15. A golf ball according to claim 14 wherein the primer is selected from the group consisting of epoxies and water-based acrylic or urethane polymers.

16. A golf ball according to any of claims 13 to 15 wherein said cover stock comprises a material selected from the group consisting of ionomer, balata or urethane.

17. A golf ball according to any of claims 13 to 16 wherein the coating is from 0.1 to 1.0 mil in thickness.

18. A golf ball according to any of claims 13 to 17 wherein the isocyanate-reactive modifier is selected from the group consisting of cellulosic esters, silicones, silanes, caprolactones, vinyl polymers, acrylic polymers, polyesters, and polyester-modified hydroxy functional polydimethylsiloxanes.

19. A golf ball according to any of claims 13 to 18 wherein the isocyanate is a polyisocyanate and the functionality reactive with the isocyanate is an hydroxyl group.

20. A golf ball comprising

(a) a highly resilient core having a cover stock selected from the group consising of ionomer, balata, urethane and mixtures of these;

(b) a primer layer on said cover stock; and

(c) a 0.1 to 1.0 mil thick cross-linked coating on said primer layer, wherein said coating is made by reacting, in a solvent, an equivalent weight of about 500 to about 700 of an acrylic polymer having a hydroxyl group functionality reactive with an isocyanate, an equivalent weight of about 300 to about 500 of a polyisocyanate, and an equivalent weight of about 300 to about 1500 of an isocyanate-reactive modifier effective to improve flexibility while retaining good abrasion resistance.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US92/03402

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08F 8/30
U.S. CL. 525/123

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	525/123, 329.1, 329.4, 329.9, 330.5, 452, 453 528/75; 273/62, 235R

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 3,264,272 (REES) 02 AUGUST 1966 See entire document.	1-4, 13-16, 20
Y	US, A, 3,454,280 (HARRISON) 08 JULY 1969 See entire document.	13-16, 20
Y	US, A, 3,819,768 (MOLITOR) 25 JUNE 1974 See entire document.	13-16, 20
A	US, A, 3,660,145 (JOHNSON) 02 MAY 1972 See entire document.	1-4, 13-16, 20
X	US, A, 3,841,895 (HICK) 15 OCTOBER 1974 See the Abstract; column 1, lines 29+; column 2, lines 45-52; column 3, lines 24+; column 4, lines 21+.	1-4
X Y	US, A, 3,979,540 (MOFFETT) 07 SEPTEMBER 1976 See the Abstract; column 2, lines 62+; column 3, lines 1-65; column 4, lines 1-52.	1-4 13-16, 20
A	US, A, 4,376,187 (THEODORE) 08 MARCH 1983 See entire document.	1-4, 13-16, 20

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" 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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 23 JUNE 1992	Date of Mailing of this International Search Report [2] 13 JUL 1992
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] for Rabon Sergent

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V ☒ **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE** [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter [1] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [1], specifically:

3. ☒ Claim numbers 5-12 & 17-19, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ **OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING** [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report cove [illegible] claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international [illegible] those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search [illegible] the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Search [illegible] invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

International Application No. PCT/US92/03402

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document,[16] with indication, where appropriate, of the relevant passages[17]	Relevant to Claim No[18]
A	US, A, 4,384,103 (CHATTHA) 17 MAY 1983 See entire document.	1-4, 13-16, 20
A	US, A, 4,379,906 (CHATTHA) 12 APRIL 1983 See entire document.	1-4, 13-16, 20
A	US, A, 4,452,930 (MORIARITY) 05 JUNE 1984 See entire document.	1-4, 13-16, 20
A	US, A, 4,452,963 (MORIARITY) 05 JUNE 1984 See entire document.	1-4, 13-16, 20
X	US, A, 4,524,183 (WEBER, JR.) 18 JUNE 1985 See the Abstract; column 1, lines 45+.	1-4
X	US, A, 4,656,237 (WEBER, JR.) 07 APRIL 1987 See the Abstract; column 1, lines 50+; column 2; column 3, lines 1-15.	1-4
A	US, A, 4,727,099 (VASTA) 23 FEBRUARY 1988 See entire document.	1-4, 13-16, 20
A	US, A, 4,758,625 (BOYACK) 19 JULY 1988 See entire document.	1-4, 13-16, 20
X	US, A, 4,814,382 (HOY) 21 MARCH 1989 See the Abstract; column 4, lines 15+; columns 5-8; column 9, lines 1-25.	1-4
P,A	US, A, 5,098,952 (BLASKO) 24 MARCH 1992 See entire document.	1-4, 13-16, 20
P,A	US, A, 5,098,956 (BLASKO) 24 MARCH 1992	1-4, 13-16, 20