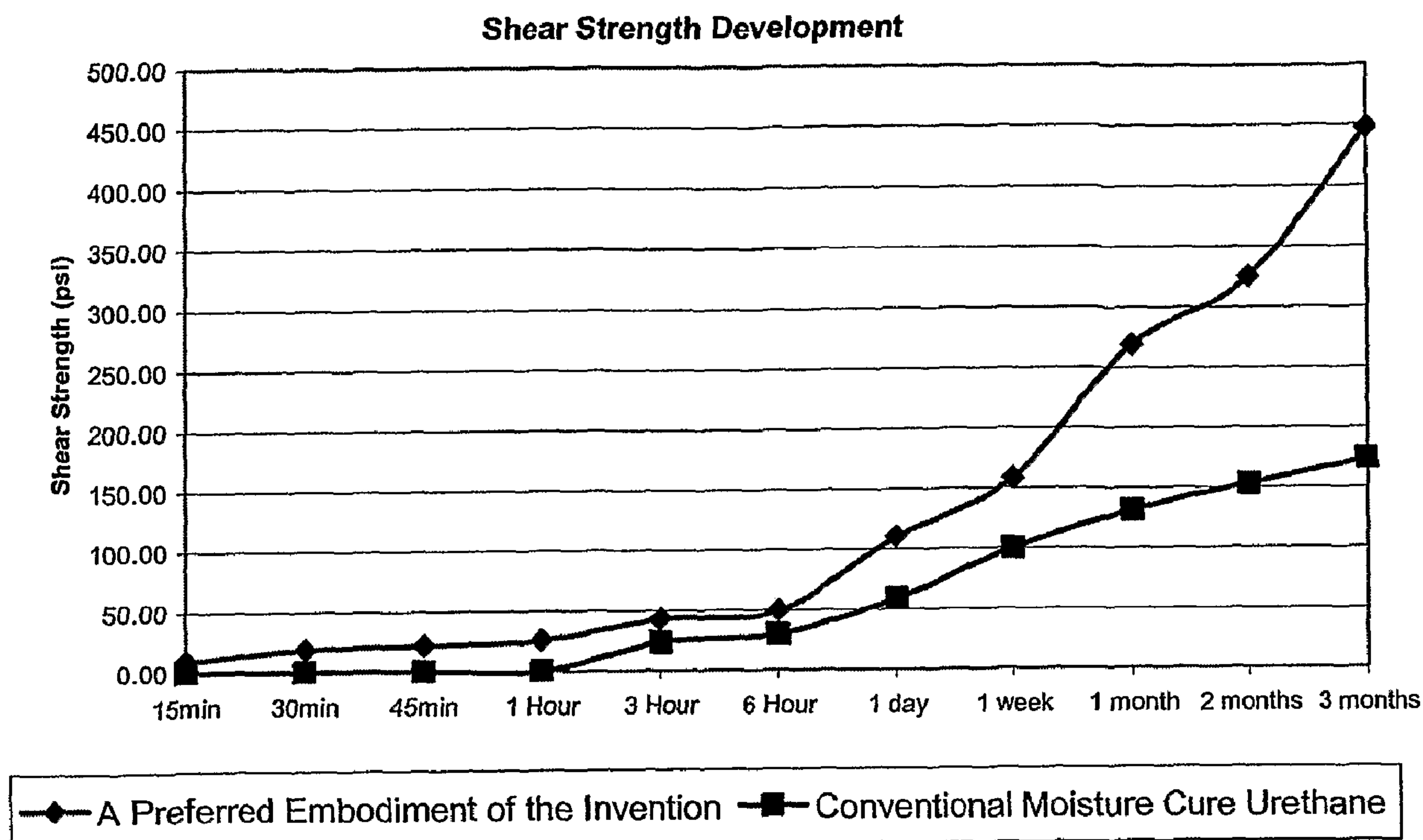




(86) Date de dépôt PCT/PCT Filing Date: 2005/02/17
(87) Date publication PCT/PCT Publication Date: 2006/06/01
(45) Date de délivrance/Issue Date: 2015/04/21
(85) Entrée phase nationale/National Entry: 2007/05/23
(86) N° demande PCT/PCT Application No.: US 2005/005077
(87) N° publication PCT/PCT Publication No.: 2006/057654
(30) Priorité/Priority: 2004/11/24 (US10/996,481)

(51) Cl.Int./Int.Cl. *C08K 5/16* (2006.01)
(72) Inventeurs/Inventors:
DDAMULIRA, ROBERT KINTU, US;
RAIDY, JOHN EDMUND, JR., US;
WRIGHT, BARRY KENNETH, US;
REGIS, DARWIN CARLES, US
(73) Propriétaire/Owner:
W.F. TAYLOR CO., INC., US
(74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : ADHESIF MONOCOMPOSANT A FAIBLES EMISSIONS
(54) Title: LOW EMISSIONS ONE PART ADHESIVE



(57) Abrégé/Abstract:

An adhesive composition which can be formulated to have low or substantially no VOC emissions is provided. Adhesives in accordance with the invention can be formulated as high solids, one-part, reactive, cross-linked adhesives. This can be achieved by utilizing amide-ester-acrylate reactions or reactions with any other carboxylated polymers. Adhesive compositions in accordance with the invention can include oils, such as various drying oils and similarly acting polymers, co-polymers, and fatty acids. Adhesives in accordance with the invention can also include various hydrocarbon resins, particularly crosslinkable hydrocarbons having a melting point in the range 70°C to 140°C. Cross-linking agents, such as materials with pendant oxazoline groups are also advantageously included. Various other mixing, flow and other handling ingredients can also be included.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
1 June 2006 (01.06.2006)

PCT

(10) International Publication Number
WO 2006/057654 A1(51) International Patent Classification:
C08K 5/16 (2006.01)Spring Drive, Roswell, GA 30075 (US). **REGIS, Darwin, Carles** [US/US]; 5612 Pimenta Avenue, Lakewood, CA 90712 (US).(21) International Application Number:
PCT/US2005/005077(74) Agents: **SIEGAL, Matthew, W.** et al.; Stroock & Stroock & Lavan LLP, 180 Maiden Lane, New York, NY 10038 (US).(22) International Filing Date:
17 February 2005 (17.02.2005)(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

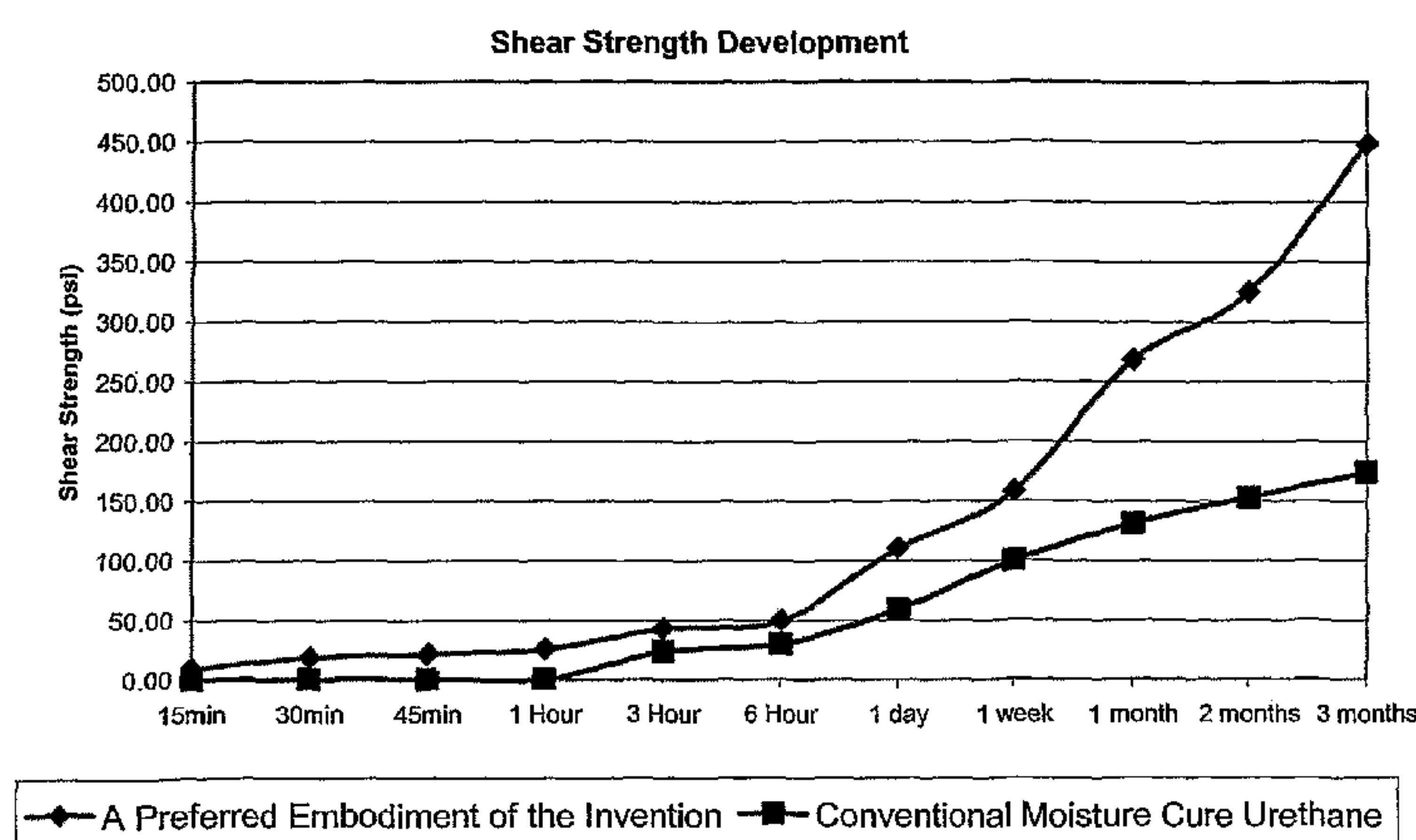
(30) Priority Data:
10/996,481 24 November 2004 (24.11.2004) US(71) Applicant (*for all designated States except US*): **W.F. TAYLOR CO., INC.** [US/US]; 11545 Pacific Avenue, Fontana, CA 923379 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **DDAMULIRA, Robert, Kintu** [CA/US]; 3900 Megan Court, Chattanooga, TN 37421 (US). **RAIDY, John, Edmund, Jr.** [US/US]; 790 Prospect Blvd., Pasadena, CA 91103 (US). **WRIGHT, Barry, Kenneth** [US/US]; 11720 Wildwood(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: LOW EMISSIONS ONE PART ADHESIVE



(57) **Abstract:** An adhesive composition which can be formulated to have low or substantially no VOC emissions is provided. Adhesives in accordance with the invention can be formulated as high solids, one-part, reactive, cross-linked adhesives. This can be achieved by utilizing amide-ester-acrylate reactions or reactions with any other carboxylated polymers. Adhesive compositions in accordance with the invention can include oils, such as various drying oils and similarly acting polymers, co-polymers, and fatty acids. Adhesives in accordance with the invention can also include various hydrocarbon resins, particularly crosslinkable hydrocarbons having a melting point in the range 70°C to 140°C. Cross-linking agents, such as materials with pendant oxazoline groups are also advantageously included. Various other mixing, flow and other handling ingredients can also be included.

WO 2006/057654 A1

WO 2006/057654 A1



Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

[001] **LOW EMISSIONS ONE PART ADHESIVE**

FIELD OF THE INVENTION

[002] The invention relates generally to low emission one part adhesives and methods of making the same, and more particularly to adhesives, such as flooring adhesives, that have low emissions of undesirable materials, such as volatile organic compounds (VOCs).

BACKGROUND OF INVENTION

[003] Many products are assembled using adhesives. For example, various flooring products made from wood, vinyl, tile, carpet and so forth are permanently adhered to a surface or substrate through the use of an adhesive. Commonly used adhesives include those sold under the trademarks Taylor Envirotec 2090 Vinyl Adhesive and Taylor Envirotec 2055 Premium Carpet Adhesive sold, by W.F. Taylor Co. of Fontana, California.

[004] There are at least two general types of adhesives: two component adhesives and one component adhesives. Two components reactive adhesives are generally formed with a resin component and a hardener component and the resin and hardener are mixed immediately prior to application. This causes a chemical reaction to occur which typically initiates some type of cross-linking process. Two component adhesives are often considered undesirable because considerable mixing of the components must occur just prior to use. This can be inconvenient. Also, just the right amount of adhesive must be mixed prior to application. If too much is mixed, or the working "pot" time is exceeded, the adhesive will harden and the excess must be discarded. Reactive urethane type adhesives contain materials such as isocyanates, which are often considered undesirable.

[005] Single component adhesives can be more convenient to use than two component adhesives. Many single component adhesives are solvent-based adhesives in which an adhesive composition is mixed with a solvent and packaged in a drum, can or tube.

After the adhesive is applied to a substrate, the solvent evaporates, which causes the adhesive to cure.

[006] The solvents used in certain conventional solvent-based adhesives are believed by some to be undesirable. Solvents commonly used in construction and flooring adhesives include, but are not limited to, acetone, cyclohexane, methyl ethyl ketone, perchloroethylene, toluene, trichloroethylene and xylene. These solvent-based adhesives are undesirable because they emit VOCs. Depending on the working environment, available ventilation, and the amount of adhesive to be used, some consider the VOC's and other emitted chemicals to be disadvantageous. Other single component adhesives contain excessive amounts of water, which can damage wood surfaces. There are other single component reactive adhesives such as moisture cure urethanes, but they typically exhibit emission problems because they give off solvents and other potentially dangerous materials including isocyanates such as toluene diisocyanate and methylene bisphenyl diisocyanate, which are considered to pose a substantial risk of serious or fatal respiratory disease.

[007] Accordingly, it is desirable to provide an improved adhesive which overcomes drawbacks and inadequacies of conventional adhesives.

SUMMARY OF THE INVENTION

[008] Generally speaking, in accordance with the invention, a one component high strength adhesive composition which can be formulated to have low or substantially no VOC emissions is provided. Adhesives in accordance with the invention can be formulated as high solids, one-part, reactive, cross-linked adhesives. This can be achieved by utilizing amide-ester-acrylate reactions or reactions with any other carboxylated polymers. Adhesive compositions in accordance with the invention can include a viscous mixture of drying oil, such as renewable soybean oil, linseed oil and sunflower oil, inorganic fillers, renewable

tackifiers such as rosins, polymers with carboxyl and/or hydroxyl functionality, metal catalysts and a non-toxic cross-linking agent.

[009] Adhesives in accordance with the invention can also include various hydrocarbon resins, particularly crosslinkable hydrocarbons having a melting point in the range 70°C to 140°C. These can be dissolved or otherwise mixed in the drying oil component. For example, C-5 hydrocarbon resins formed from hydrocarbons having an average of about five carbon atoms and C-9 hydrocarbon resins formed of hydrocarbons having an average of about 9 carbon atoms and preferably both, mixed in effective proportions to provide desired cured strength, green strength, open working times and so forth can be satisfactory.

[0010] Adhesives in accordance with the invention can also include fugitive alkali agents, such as ammonia, monomethanol amine (MEA) and triethanol amine (TEA). Cross linking agents, such as Oxazoline with pendant groups; n-Methylol acrylamide; Glycidyl methacrylate; 3-Methacryloxypropyl-Trimethoxysilane; 3-Mercaptopropyl Trimethoxysilane; Polyvalent metal carboxylate salts; Diacetone acrylamide; Acid diahydrazide; Adipic dihydrazide; DAAM/Glyoxal; Urea/Glyoxal; Carbodiimide functionalized material such as polycarbodiimides and carbodiimide; Epoxy functional water miscible/emulsifiable additives such as aziridine; Metal ionic cross-linkers, such as zirconium, zinc, calcium; Polyisocyanates; Organosilanes, Urea formaldehyde/melamine formaldehyde resins; Aziridine functionalized materials and Polyethylenimine are also advantageously included. Various other mixing, flow and other handling ingredients can also be included.

[0011] High solids construction adhesives in accordance with the invention can be particularly useful in assembling various flooring products made from wood, vinyl, ceramic, rubber to various substrates common to flooring installations including: concrete, plywood, underlayment grade particle board, vinyl, ceramic tile, cement patches and underlayments,

radiant heat flooring and terrazzo. Adhesives in accordance with the invention can benefit from polymer emulsions with carboxyl functionality, polymer emulsion cross-linkers containing pendant oxazoline group are also advantageously employed. Other useful ingredients include tackifying hydrocarbon resins dissolved in drying oils; naphthanates of metals such as cobalt, calcium, zirconium, and manganese; fugitive bases for pH adjustment; and other stabilizing agents, such as fugitive anti-oxidants.

[0012] The initial chemical reactions involved in the curing process of the adhesive in accordance with the invention are believed to be mainly a result of autoxidation of the drying oil. The process is believed to involve formation of hydroperoxide-substituted fatty acids and breakdown of the hydroperoxides, giving rise to highly reactive radicals and subsequent cross-linking. The cross-linking reaction can be catalyzed by the presence of transition metals. The resulting cross-linked bonds can be covalent ethers, peroxide and carbon-carbon bonds. As the cross-linking proceeds and the adhesive solidifies, a three-dimensional network can be formed when there is more than one reactive site on the unsaturated fatty acids in the drying oil, hence more than one point to create a cross-link bond.

[0013] Accordingly, it is an object of the invention to provide an improved adhesive.

[0014] Another object of the invention is to provide an improved method of making an adhesive.

[0015] Still other objects of the invention will in part be obvious and will, in part, be apparent from the specification. The invention accordingly comprises the composition of matter, the method of making a composition of matter and the method of using the composition of matter which will be exemplified in the compositions and methods hereinafter described, and the scope of the invention will be indicated in the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] In the drawing figures, which are merely illustrative:

[0017] FIG. 1 is a graph depicting shear strength development over three months aging, comparing the performance of a preferred embodiment of the invention with a leading moisture cure urethane adhesive on the market. As demonstrated in FIG. 1, an adhesive in accordance with the preferred embodiments of the invention is immediately stronger than a leading moisture cure urethane adhesive, cures to have higher shear strength and does not give off unacceptable VOCs while curing.

[0018] FIG. 2 is a graph showing increase in cross link density of an adhesive formulated in accordance with a preferred embodiment of the invention, with progressing time.

[0019] FIG. 3 depicts a fresh un-reacted adhesive film.

[0020] FIG. 4 depicts a partially cross-linked film.

[0021] FIG. 5 depicts a fully cross-linked adhesive.

[0022] FIGS. 3-5 are schematic models depicting different stages in the developing of the three dimensional network of cross-linked bonds in an adhesive based on drying oils.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] The invention is directed to adhesive compositions and methods of making adhesive compositions which can include ingredients set forth below. The invention also relates to methods of applying flooring involving the use of those adhesives. As will be evident to those of ordinary skill in the art, substitutions, omissions and additions will be possible in order to provide adhesives with customized selected properties.

[0024] Preferred ingredients, preferred percentages of components and mixing processes in accordance with preferred embodiments of the invention will be set forth below in Table 1.

TABLE 1

<u>Preferred Ingredient</u>		<u>Preferred Amount</u> <u>wt %</u>	<u>Preferred Process</u>
1	Drying Oils such as Linseed Oil, Tung Oil, Sunflower Oil, Cashew Shell Oil, Castor Oil, Coconut Oil, Cotton Seed Oil, Fish Oil, Oiticica Oil, Rapeseed Oil, Safflower Oil, Sesame Oil, Soybean Oil, Walnut Oil, Synthetic Drying Oils, Tall Oil, Fatty Acids, or any blend of the above.	4 to 10	
2	Aliphatic C-5 Hydrocarbon Resin with a softening point of between about 75° and 115°C, such as that produced from Acyclic Aliphatic monomers such as Cis 1, 3 Pentadiene, Trans 1, 3 Pentadiene, 2-Methyl 2 Butene, Dicyclopentadiene Copolymers, Vinyltoluene Copolymers	4 to 10	
3	Alkylated Aromatic C-9 Resin with a softening point of between about 100° and 140°C, produced from C-8 to C-10 monomers such as Styrene, Vinyl Toluene, Indene, Methyl Indene, Alpha Methyl Styrene.	10 to 20	Ingredient 2 and 3 are combined with Ingredient 1. Temperatures of between about 240° and 300°F may be required to form a substantially homogenous solution. This homogenous solution should be held at between about 250° and 260° before being combined with the ingredients below.
4	Surfactants, such as 6 to 10 mole ethoxylates of nonylphenols and other emulsifying agents such as saponified esters.	0.50 to 1.50	Add ingredients 4 and 5 to ingredient 6 while mixing until uniform.
5	Anti-foaming agents such as non-silicon anti-foaming agents	0.05 to 0.10	

<u>Preferred Ingredient</u>		<u>Preferred Amount</u> <u>wt %</u>	<u>Preferred Process</u>
6	Polymer emulsions or hot melt polymers (advantageously high solids) with carboxyl functionality, such as Acrylic, Styrene Butadiene, EVA, VAE	30 to 60	Maintain the temperature of ingredient 6 to between 60° and 90° F. Add ingredients 4 and 5 while mixing until uniform. Then add the premixed ingredients 1, 2 and 3 above to ingredient 6 with high shear agitation until ingredients form a homogenous emulsion.
7	Fugitive anti-oxidants such as oximes such as methyl ethyl ketoxime, Bactericide, Fungicides, and Freeze-Thaw Stabilizers	0.10 to 1.00	Add while agitating
8	Fugitive alkali agent, such as Ammonia, MEA, TEA	0.10 to 1.00	Use the alkali to adjust the above emulsion pH to between 8-10 before adding ingredients 9 and 10
9	Dispersing Agent, such as salts of poly acrylic acid	0.10 to 1.00	Add while agitating
10	Napthanates of metals such as cobalt, calcium, zirconium, and manganese	0.10 to 1.00	Add while agitating
11	Polymer emulsion with pendant oxazoline groups or other suitable cross-linking agent	1.00 to 7.00	Add while agitating
12	Fillers such as Calcium Carbonate, Kaolin Clay, Mica, Talc, Silica, etc.	20 to 40	Add slowly with high shear agitation

[0025] Adhesive compositions in accordance with the invention advantageously include liquids that can be used to dissolve and blend other ingredients, but which can be easily and readily oxidized and/or polymerized to transform into a hard, dry material after exposure to air. Examples of such material include relatively highly unsaturated oils and polymers, such as those identified above as drying oils. The drying oil component can be included as about 1 to 20%, preferably 4 to 10%, more preferably about 2% to 5%. By

dissolving (mixing) the resins in the drying oil component and the addition of fugitive anti-oxidants, the resins can be prevented from cross-linking until the drying oil is exposed to air and hardens. The cross-linking starts as the composition starts to dry and the fugitive anti-oxidant starts to evaporate. Thus, there should be sufficient anti-oxidant to prevent the composition from curing too quickly, and to provide sufficient open time and ease of handling. Preferred open time should be up to about 30 and sometimes up to about 60 minutes and depend on the desired application.

[0026] Adhesives in accordance with the invention can also include hydrocarbon resins. The resins are selected to give the cured adhesive the desired amount of cured strength. Appropriate selection of resins also affects the uncured strength (initial shear strength) of the adhesive, often referred to as green strength. For example, if the adhesive is used as a flooring adhesive, it is desirable that the uncured adhesive maintain the applied flooring in place with reasonable security so that tiles, for example, can be aligned properly and so that minor bumps and nudges do not require reseating and realignment of the flooring materials. Below in Table 2 is a comparison of typical green strength in psi, of adhesives in accordance with a preferred embodiment of the invention compared to a leading VOC emitting Moisture Cure Urethane Adhesive currently on the market:

TABLE 2

Cure Time	15 Min	30 Min	45 Min	60Min	3 Hour	6 Hour	16 Hour	24 Hour
Invention Adhesive	5	22	23	32	45	50	86	94
Moisture Cure Urethane	1	1	1	1	7	28	53	57

Cure Time	1 week	1 month	2 months	3 months
	158	269	325	448
Moisture Cure Urethane	100	132	153	174

[0027] Conventional moisture Cure Urethane adhesives can contains up to 1% 4,4'-Diphenylmethane Diisocyanate (MDI), up to 1% Toluene Diisocyanate, up to 10% Aliphatic Petroleum Distillates, up to 1% Ethyl Benzene, Up to 5% Xylene, Up to 7% Mineral Spirits

and up to 1.5% 1,2,4-Trimethyl Benzene. All these VOCs are listed in the hazardous materials section of the MSDS for most commercial grade moisture cure urethane adhesives.

[0028] It has been determined that the cured strength and green strength of the adhesive can be related to the softening points of the resin material. As used herein, softening point will refer to the temperature at which viscous flow of a material that does not have a definite melting point changes to plastic flow.

[0029] Resins in accordance with preferred embodiments of the invention generally have softening points between 75°C and 140°C. It has also been determined that by mixing resins with different softening points, advantageous characteristics of each resin can be realized. For example, resins with a relatively low softening point, e.g., about 95-105°C will have up to 30-40% less green strength and cured strength than resins with a relatively high softening point in the range of e.g., 115-130°C. Softening point also affects processing and handling properties. If a softening point is too high, desired materials might be difficult to emulsify at temperatures needed for proper mixing.

[0030] In one embodiment of the invention, a resin formed with hydrocarbons having, on average, 6 or fewer carbon atoms and a softening point preferably between 75°C and 115°C is combined with a relatively harder resin formed from hydrocarbons having an average of 7 or more carbon atoms and a softening point preferably about between 100°C and 140°C.

[0031] In preferred embodiments of the invention, the relatively soft resin is an aliphatic hydrocarbon resin formed of hydrocarbons having an average of about 5 carbon atoms. Advantageous resins can be formed from acyclic aliphatic monomers, such as cis 1, 3 pentadiene, trans 1, 3 pentadiene, and 2-methyl 2 butene and cyclopentadienes.

[0032] Adhesive compositions in accordance with the invention also advantageously include a relatively harder hydrocarbon resin, particularly one having a higher temperature

WO 2006/057654

PCT/US2005/005077

softening point in the range of 100°C to 140°C. In particular, alkylated aromatic resins, particularly those formed from hydrocarbons having an average of 8 to 10 carbon atoms, such as those produced from C-8, C-9 and C-10 monomers, such as styrene, vinyl toluene, indene, methyl indene, alpha methyl styrene. Particularly suitable C-9 resins include petroleum aromatic hydrocarbon resins having softening points in the range 100°C to 135°C. These relatively harder resins are advantageously included as 10 to 20%, preferably 12% to 18%.

Other non-limiting examples of suitable C-9 and C-5 Resins are described below in Table 3.

Adhesives in accordance with the invention can also be formulated with Versadil 100,TM
Versadil 101 and Versadil 200.TM

TABLE 3

Manufacturer	C-9 Resins	C-5 Resins
Rutgers VFT AG Varziner Strasse 49, D-47138 Duisburg Germany	• Novares TT120 • Novares TT130	
Sartomer Company Oaklands Corporate Center 502 Thomas Jones Way Exton, PA 19341	• Norsolene S115,TM • Norsolene S125, • Norsolene S135	
Exxon Chemicals Houston 2401 S. Gessner Houston, TX 77063-2005, USA		• Escorez 1102TM • Escorez 1304 • Escorez 1310LC • Escorez 1315 • Escorez 1580
Neville Chemical Company 2800 Neville Road Pittsburgh, PA 15225	• Nevchem 110TM • Nevchem 120 • Nevchem 130 • Nevex 100	• LX-1200 • LX-1200-130 • LX-2600-125
Eastman Chemical Company P.O.Box 431 Kingsport, TN 37662	• Petrorez 100TM • Petrorez 199 • Petrorez 200	
Resinall 3065 High Ridge Road P.O. Box 8149 Stamford CT 06903	• Resinall 711TM • Resinall 717 • Resinall 736 • Resinall 737 • Resinall 747 • Resinall 771 • Resinall 774	Resinall 769
TOSOH Corporation Suite 600, 1100 Circle 75 Parkway, Atlanta, GA 30339-3097, U.S.A.	• Petcoal@ 100 • Petcoal@ 120 • Petcoal@ 120HV • Petcoal@ 140	
Arakawa CHEMICAL (USA) INC. 625 N. Michigan Avenue - Suite #1700 Chicago, IL 60611 USA	• Arkon SM-10TM • Arkon SP10	

WO 2006/057654

PCT/US2005/005077

Grenhall Chemicals Limited 7686 Bath Road, Mississauga, ON Canada L4T 1L2	• Resin GC100, • Resin GC300, • Resin GC400	
Hercules Inc. Resins Division Hercules Plaza 1313 North Market Street Wilmington, DE 19894	• Picco 5120TM • Picco 6115	• Piccotac 115TM • Piccotac B
Yuen Liang Industrial Co., Ltd South Korea	Petroresin (yl-series, sk-series, <u>gs</u> -series b-series with softening point of between 90 -130° C	
Sunbelt Chemicals, Inc. 407 N. Cedar Ridge, Suite 230 Duncanville, Texas 75116	• SB1000 • SB1100 • SB140ESTM	• R100AS • S105A • R100G
LUKOIL Bulgaria Bulgaria 1421 Sofia, 59 A Cherni Vrah Blvd	• PYROLEN 100TM	

[0033] When preparing adhesive compositions in accordance with the invention, the low softening point resins (with 6 or fewer carbon atoms) are advantageously provided in the drying oil component in about a 2:1 to 1:2, preferably 1:1 weight ratio. The mixture of ingredients 1 and 2 of Table 1 can then be advantageously heated to a temperature above the softening point of the high temperature resin, preferably in the range of 115°C to 140°C with mixing, to form a generally homogeneous combination. Care should be taken to insure that the composition is not heated to a temperature too far over the softening points of the materials or it can be difficult to blend with the rest of the ingredients. Thus, after a homogeneous combination is achieved, the temperature can be reduced to a point when ease of mixing is maintained, generally approximately 115°C to 130°C.

[0034] Surfactants, such as 6 to 10 mole ethoxylates of nonylphenols can be included, advantageously in the range of less than 5% by weight, advantageously 0.5 to 1.5%.

[0035] It is also advantageous to include anti-foaming agents, in particular, non-silicon anti-foaming agents. These are advantageously included as less than about 0.5 weight percent, preferably 0.05 to 0.10 weight percent.

[0036] Adhesives in accordance with the invention also advantageously include polymer emulsion materials, particularly those having carboxyl functionality to provide enhanced adhesive properties, such as those having acrylic, styrene butadiene, ethylene vinyl acetate copolymer (EVA) and vinyl acetate ethylene copolymer can be included as about 20 to 80%, preferably about 30 to 60%, more preferably about 35 to 55% of the composition. The emulsion should be maintained at a temperature of about 15 to 30°C. Ingredients 4 and 5 can then be added and mixed until uniform. Ingredients 1, 2 and 3 are then added with high shear agitation until the ingredients form a substantially homogeneous blend.

[0037] Compositions in accordance with the invention also advantageously include fugitive anti-oxidants, such as oximes, such as methyl ethyl ketoxime, bactericides, fungicides and freeze/thaws stabilizers.

[0038] Compositions in accordance with the invention also advantageously include fugitive alkali agents, such as ammonia, monomethanol amine (MEA) and triethanolamine (TEA). This alkali agent can be useful to adjust the pH of the emulsion to at least 7, preferably between about 8 and 10 before the oxazoline containing component is added.

[0039] Adhesive compositions in accordance with the invention can also include up to 2%, preferably 2.1 to 1% dispersing agents, such as salts of polyacrylic acids and dryers, in particular naphthanates of metals, such as cobalt, calcium, zirconium and manganese. The dryers should be included in an effective amount to catalyze the drying speed of the drying oil to a desired rate. The precise amount will depend on both the desired speed of cure and the particular composition of the adhesive. These should be added with agitation.

[0040] Adhesive compositions in accordance with the invention also advantageously include cross-linking agents. Preferred cross-link agents include: oxazole containing materials, in particular, polymer emulsion materials that include pendant oxazoline groups; 3-methacryloxypropyl-trimethoxysilane (MEMO); 3-mercaptopropyl trimethoxysilane

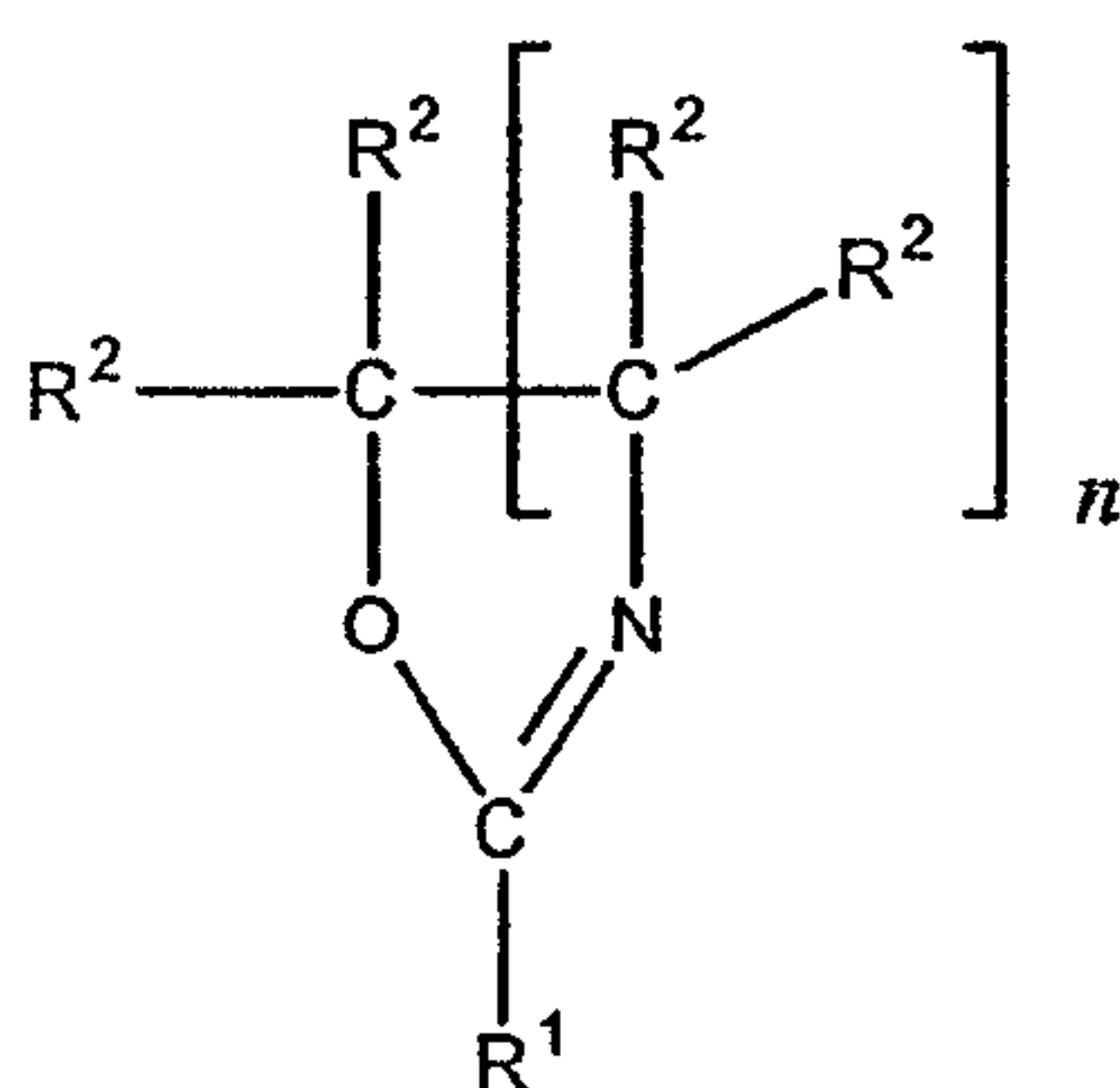
WO 2006/057654

PCT/US2005/005077

(MTMO); glyoxal such as DAAM/glyoxal or urea/glyoxal; epoxy functional, water miscible/emulsifiable additives such as aziridine; polyvalent metal carboxylate salts or metal ionic cross-linkers, such as zirconium, zinc, calcium; carbodiimide functionalized material such as polycarbodiimides and carbodiimide; polymerizable organosilanes; aziridines functionalized materials. Other likely crosslinkers include n-methylol acrylamide, glycidyl methacrylate, acid dihydrazide such as diacetone acrylamide or adipic dihydrazide, and water dispersible polyisocyanates

[0041] When oxazoline with pendant groups act as the cross-linking agents, there should preferably be about a 1:1 mole ratio between carboxy groups in the composition and oxazoline groups. If too much of these materials are added, it will lower the possible solids content. If too little is added there will be lower cross link density and a weaker adhesive.

[0042] Oxazolines are 5-membered heterocyclic compounds, having the general formula C_3H_3NO and are frequently used in organic synthesis. Emulsions containing particles of an oxazoline-modified polymer containing pendant oxazoline groups are discussed in U.S. Patent Nos. 4,474,923, 4,508,869 and 4,325,856. Preferred oxazolines have the following formula:



[0043] wherein R^1 is an acyclic or organic radical having addition polymerizable unsaturation; each R^2 is independently hydrogen, halogen or an inertly substituted, organic

radical and n is 1 or 2. The oxazoline containing emulsion preferably also includes at least one other addition polymerizable monomer which is copolymerizable with the oxazoline and discrete particles of a coreactive polymer which coreactive polymer had been prepared in an emulsion polymerization process from (1) an addition, polymerizable coreactive monomer containing pendant groups which are capable of reacting with an oxazoline group to form covalent bonds thereto and (2) at least one other monomer which is copolymerizable with said coreactive monomer.

[0044] Adhesive compositions in accordance with the invention can also include effective amounts of fillers, such as calcium carbonate, kaolin clay, mica powder, talc and so forth. Fillers should generally represent less than 50% of the composition, preferable in the range of 20-40% of the composition. If too much filler is included the cohesive strength of the product can be reduced. If too little filler is included, the solids content will be too low for many applications.

[0045] These components should be added slowly, with high shear agitation, to ensure a substantially homogeneous mixture.

[0046] After adhesive compositions in accordance with the invention are deposited, the polymer emulsion containing the oxazoline groups is believed to become available to act as a cross-linking agent to cure the carboxylated polymers. Accordingly, a one component self-curing adhesive which can be made substantially or entirely free of VOC's can be achieved.

[0047] In another non-limiting embodiment of the invention, the process by which the adhesive in accordance with the invention is made can be split into two stages. The first stage can comprise the blending of the first seven ingredients and storing, with constant slow agitation, the resulting mixture as a premix to be used the final blend. The second stage comprises blending the last five ingredients with the premix.

[0048] Prior to blending the premix with the remaining ingredients, the premix may be cooled to a temperature preferable in the range of 75°F to 110°F. The cooling may occur using such devices as: a cooling jacket with cold water, a cooling jacket with a cooling tower, heat exchanger, a flash vacuum cooling system, or any other cooling device that can lower the temperature to within the desired range. Heat exchangers such as shell and tube heat exchangers, spiral heat exchangers, plate and frame heat exchangers, or compabloc welded plate heat exchangers may be used.

[0049] After blending the premix with the remaining ingredients and prior to packaging the composition, the final temperature of the batch should be cooled to a temperature of preferably not more than 90°F.

[0050] Areas designed to house electrical equipment or various manufacturing or testing procedures often need to avoid the build-up of static electricity. In another non-limiting embodiment of the invention, adhesives in accordance with the invention can be rendered electrically conductive. Conductive adhesive are advantageously used in constructing Electrostatic Dissipative Floors (ESD) by the inclusion of electro-conductive agents in the adhesive composition. Particularly suitable electro-conductive agents include carbon black, synthetic conductive fibers, electrically conductive metal chips or fragments, or any other conductive materials such as conductive nano materials.

[0051] Table 4, below provides formulation information for preparing electrically conductive adhesives in accordance with the invention. Table 4 also shows an alternative manufacturing process, which can also be used with the non-conductive adhesive. Other processing steps can be substituted such as those in Table 1.

TABLE 4

Conductive Adhesive

	Preferred Ingredients	Preferred Amount wt %	Preferred Process
1	Drying Oil such as Linseed oil, Tung Oil, Sunflower Oil, Cashew Shell Oil, Castor Oil, Coconut Oil, Cotton Seed Oil, Fatty Acids, Fish Oil, Oiticica Oil, Rapeseed Oil, Safflower Oil, Sesame Oil, Soybean Oil, Walnut Oil, Synthetic Drying Oils, Tall Oil, Fatty Acids,	4 to 10	
2	Aliphatic C-5 Hydrocarbon Resin with a softening point of between 75° and 115° C, such as those produced from Acyclic Aliphatic monomers such as Cis 1,3 Pentadiene, Trans 1,3 Pentadiene, 2-Methyl 2 Butene, Dicyclopentadiene Copolymers, Vinyltoluene Copolymers,	4 to 10	
3	Alkylated Aromatic C-9 Resin with a softening point of between about 100° and 140° C, produced from C8 to C-10 monomers such as Styrene, Vinyl Toluene, Indene, Methyl Indene, Alpha Methyl Styrene.	10 to 20	Ingredient 2 and 3 are dissolved in ingredients 1 at temperatures of between 240° and 300° F to form a homogenous solution. This homogenous solution should be held at between 250° and 260°F before being added to ingredients below.
4	Surfactants, such as 6 to 10 mole ethoxylates of nonylphenols.	0.50 to 1.50	
5	Anti-foaming agents, such as Non-Silicon Anti-foaming agents	0.05 to 0.10	Ingredients 1 through 5 should be premixed and then heated and maintained at temperature between about 240° and 260° F.
6	Polymer emulsion, advantageously with high solids content, e.g. Latex Polymer with Carboxyl Functionality, such as Acrylic, Styrene Butadiene, EVA, VAE.	30 to 60	Pre-heat and maintain the temperature of ingredient 6 to between 60° and 100° F. Add the premixed ingredients above to ingredient 6 with high shear agitation until ingredients form a homogenous emulsion.
7	Fugitive anti-oxidants, Bactericide, Fungicides, and Freeze-Thaw Stabilizers	0.10 to 1.00	Add while agitating

Stage one is the blending of the first 7 ingredients and storing preferably (with constant slow agitation). The resulting mixture is used as a premix to be used in the final blend. Prior to blending the premix above with the rest of the ingredients below, the premix should be coded.

8	Dispersing Agent, such as salts of poly acrylic acid.	0.10 to 1.00	Add while agitating
9	Electro-conductive agents such as; Carbon black, Synthetic Conductive Fibers, Electrically Conductive metal chips or fragments, or any other conductive materials such as Conductive Nano Materials	5.0 to 15.0	Add while agitating
10	Napthanates of metals such as cobalt, calcium, zirconium, and manganese	0.10 to 1.00	Add while agitating
11	Fugitive alkali agent, such as Ammonia, MEA, TEA	0.10 to 1.00	Use the alkali to adjust the above emulsion pH to between 8-10 before adding ingredients 9 and 10
12	Fillers such as Calcium carbonate, Kaolin Clay, Mica, Talc etc	20 to 40	Add slowly with high shear agitation
13	Latex polymer emulsion with pendant oxazoline groups	1.00 to 7.00	Add while agitating

The final temperature of the batch should be cooled to a temperature of not more than 90°F, prior to packaging.

[0052] The following examples are provided for purposes of illustration only and should not be construed as limiting the scope of the invention.

TABLE 5

Shear Strength Data (psi) at various Cure Times

	15 Min	30 Min	45 Min	1 Hour	3 Hour	6 Hour	16 Hour	24 Hour
Example 1	4.3	11.6	26.2	29.8	45.3	50.3	86.6	94.0
Example 2	4.1	20.7	23.3	29.4	38.9	43.2	81.5	89.1
Example 3	4.9	21.7	23.3	31.5	45.3	50.3	85.7	94.0
Conventional Moisture	1	1	1	1	7	28	53	57

Cure Urethane								
------------------	--	--	--	--	--	--	--	--

[0053] As shown in Table 5, the adhesive of Examples 1-3, set forth below, exhibited excellent green strength and cure strength compared to conventional adhesives such as moisture cure urethane and exhibited acceptably low VOC emissions while curing.

[0054] Table 6, below, provides non-limiting examples of application examples. As shown, adhesive in accordance with the invention can be used to apply a wide variety of flooring. Acceptable coverage depends on the underlying floor substrate and the backing of the flooring to be applied. However, coverage in the range of about 20 to 300 ft²/gallon can be acceptable, preferably about 20-150 ft²/gallon for wood; 100-300 ft²/gallon for vinyl or ceramic and 50-150 ft²/gallon for carpet. The adhesive can be applied using any suitable dispensing method such as trowelling, spray pumping, extrusion and so forth.

TABLE 6

Application Devices and Application Rates

Installation Application	Trowel Size (width x depth x spacing)	Coverage (square feet per gallon)
Carpet or Wood	3/32" X 3/32" X 3/32" v notch	100 – 120
Carpet	1/8" x 1/8" x 1/16" v notch	75 – 108
Carpet	1/8" x 1/8" x 1/16" u notch	36 – 63
Vinyl	1/16" x 1/16" x 1/16" sq. notch	150 – 180
Vinyl	1/16" x 1/32" x 1/32" u notch	180 – 250
Wood	1/8" x 1/8" x 1/8" sq. notch	60 – 80
Wood	3/16" x 3/16" x 3/16" sq. notch	30 – 40
Wood	3/16" x 1/4" x 1/2" V notch	50 - 60

Example 1 - Construction Adhesive

	Ingredient	Amount wt %	Process
1	Linseed Oil	6.00	
2	Aliphatic C-5 Hydrocarbon Resin with a softening point of 85° C	6.00	
3	Alkylated Aromatic C-9 Resin with a softening point of 115° C	14.25	Ingredient 2 and 3 are dissolved in ingredients 1 at temperatures of between 240° and 300° F to form a homogenous solution. This homogenous solution should be held at between 250° and 260° F before being added to ingredients below.
4	9 mole ethoxylates of nonylphenols surfactant	1.00	Add ingredients 4 and 5 to ingredient 6 while mixing until uniform.
5	Non-Silicon Anti-foaming agent	0.25	
6	Carboxylated High Solids Acrylic	43.00	Maintain the temperature of ingredient 6 to between 60° and 90° F. Add ingredients 4 and 5 while mixing until uniform. Then add the premixed ingredients 1, 2, and 3 above to ingredient 6 with high shear agitation until ingredients form a homogenous emu
7	Fugitive anti-oxidant, and Freeze-Thaw Stabilizer	0.05	Add while agitating

7	Bactericide, and Fungicides	0.05	Add while agitating
8	Ammonia	0.50	Use the alkali to adjust the above emulsion pH to between 8-10 before adding ingredients 9 and 10
9	Dispersing Agent, such as salts of poly acrylic acid.	0.20	Add while agitating
10	Cobalt, Managanese, and Manganese Napthanates	0.20	Add while agitating
11	Polymer emulsion with pendant oxazoline groups	1.50	Add while agitating
12	Calcium Carbonate	27.00	Add slowly with high shear agitation

Example 2 for Construction Adhesives

	Ingredient	Amount wt %	Process
1	Tung Oil	6.00	
2	Aliphatic C-5 Hydrocarbon Resin with a softening point of 85° C	6.00	
3	Alkylated Aromatic C-9 Resin with a softening point of 115° C	14.25	Ingredient 2 and 3 are dissolved in ingredients 1 at temperatures of between 240° and 300° F to form a homogenous solution. This homogenous solution should be held at between 250° and 260° F before being added to ingredients below.
4	9 mole ethoxylates of nonylphenols surfactant	1.00	Add ingredients 4 and 5 to ingredient 6 while mixing until uniform.
5	Non-Silicon Anti-foaming agent	0.25	
6	Carboxylated High Solids Styrene Butadiene Rubber	43.00	Maintain the temperature of ingredient 6 to between 60° and 90° F. Add ingredients 4 and 5 while mixing until uniform. Then add the premixed ingredients 1, 2, and 3 above to ingredient 6 with high shear agitation until ingredients form a homogenous emu
7	Fugitive anti-oxidant, and Freeze-Thaw Stabilizer	0.05	Add while agitating

7	Bactericide, and Fungicides	0.05	Add while agitating
8	Ammonia	0.50	Use the alkali to adjust the above emulsion pH to between 8-10 before adding ingredients 9 and 10
9	Dispersing Agent, such as salts of poly acrylic acid.	0.20	Add while agitating
10	Cobalt, Managanese, and Manganese Napthanates	0.20	Add while agitating
11	Polymer emulsion with pendant oxazoline groups	1.50	Add while agitating
12	Calcium Carbonate	27.00	Add slowly with high shear agitation

Example 3 - Construction Adhesive

	Ingredient	Amount wt %	Process
1	Sunflower Oil	6.00	
2	Aliphatic C-5 Hydrocarbon Resin with a softening point of 85° C	6.00	
3	Alkylated Aromatic C-9 Resin with a softening point of 115° C	14.25	Ingredient 2 and 3 are dissolved in ingredients 1 at temperatures of between 240° and 300° F to form a homogenous solution. This homogenous solution should be held at between 250° and 260° F before being added to ingredients below.
4	9 mole ethoxylates of nonylphenols surfactant	1.00	Add ingredients 4 and 5 to ingredient 6 while mixing until uniform.
5	Non-Silicon Anti-foaming agent	0.25	
6	Carboxylated High Solids Styrene Butadiene Rubber	43.00	Maintain the temperature of ingredient 6 to between 60° and 90° F. Add ingredients 4 and 5 while mixing until uniform. Then add the premixed ingredients 1, 2, and 3 above to ingredient 6 with high shear agitation until ingredients form a homogenous emu

7	Fugitive anti-oxidant, and Freeze-Thaw Stabilizer	0.05	Add while agitating
8	Bactericide, and Fungicides	0.05	Add while agitating
9	Ammonia	0.50	Use the alkali to adjust the above emulsion pH to between 8-10 before adding ingredients 9 and 10
10	Dispersing Agent, such as salts of poly acrylic acid.	0.20	Add while agitating
11	Cobalt, Managanese, and Manganese Napthanates	0.20	Add while agitating
12	Polymer emulsion with pendant oxazoline groups	1.50	Add while agitating
13	Kaolin Clay	7.00	Add slowly with high shear agitation
14	Calcium Carbonate	20.00	Add slowly with high shear agitation

[0055] Table 7 below provides Moisture Transmission Data (per ASTM 96-00) of adhesive in accordance with a preferred embodiment of the invention versus leading Moisture Cure Urethane Wood Adhesive which emit undesirable VOCs.

Table 7

Adhesive	ASTM 96-00 Moisture Transmission, G/m ² (24 hr-mm Hg)
A preferred embodiment of the invention	0.59.
Commercial Moisture Cure Urethane Wood Adhesive 1	1.20.
Commercial Moisture Cure Urethane Wood Adhesive 2	0.60.

[0056] Low moisture transmission permits an adhesive to act as a moisture barrier. Table 6 shows that adhesives in accordance with the invention can be formulated to have at least as good moisture barrier properties as conventional urethane adhesives, but without the same level of VOC emissions.

[0057] FIG. 1 shows that in certain respects, adhesives in accordance with the invention can have enhanced adhesive properties compared with conventional urethane adhesives. Adhesives in accordance with the invention can be formulated to have a shear strength of over 5 psi, even over 10 psi at 15 minutes, and over 10 psi, even over 20 psi at 30 min. Final cure strengths (at 3 months) can exceed 200 psi, and can even exceed 300 psi or 400 psi. The adhesive used for FIG. 1 exhibited a shear strength of 450 psi. In addition to exhibiting advantageous green strengths, adhesives in accordance with the invention also exhibit desirable open times. Even at open times of up to 60 minutes the adhesive will still exhibit advantageous strength characteristics.

[0058] FIG. 2 shows the progression of cross-link density with time for one embodiment of the invention. Adhesives in accordance with the invention can be formulated

WO 2006/057654

PCT/US2005/005077

to exhibit an immediate initiation of cross-linking and a steady progression for the first hour.

Different embodiments of the invention can be formulated to exhibit faster or slower progressions, varying by e.g. – about 10 or 20%, or otherwise depending on the desired applications.

[0059] It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

[0060] Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such ingredients wherever the sense permits.

CLAIMS

1. An adhesive composition, comprising: the combination produced by combining 1 to 20% by weight of a drying oil component; 14 to 30% by weight of a hydrocarbon resin component; and 1 to 7% by weight of a cross-linking agent, wherein the cross-linking agent comprises at least one member selected from the group consisting of 3-methacryloxypropyl-trimethoxysilane, 3-mercaptopropyl-trimethoxysilane; polycarbodiimides; carbodiimides; n-methylol acrylamide; glycidyl methacrylate; diacetone acrylamide; and adipic dihydrazide to provide an adhesive that can be applied to a substrate and which will cure on the substrate.
2. The adhesive composition of claim 1, wherein the hydrocarbon resin component comprises 4 to 10% by weight of the composition of a first hydrocarbon resin having an average of six or fewer carbon atoms and a softening point between 75°C and 115°C, provided in the drying oil component at a weight ratio of 2:1 to 1:2; and 10 to 20% by weight of the composition of a second hydrocarbon resin having an average of seven or more carbon atoms and a softening point between 100°C and 140°C.
3. The adhesive composition of claim 1, wherein the drying oil component comprises at least one member selected from the group consisting of linseed oil, tung oil, and sunflower oil.
4. The adhesive composition of claim 1, wherein the drying oil component comprises at least one member selected from the group consisting of cashew shell oil, castor oil, coconut oil, cotton seed oil, fish oil, oiticica oil, rapeseed oil, safflower oil, sesame oil, soybean oil, walnut oil, tall oil, and fatty acids.

5. The adhesive composition of claim 2, wherein the first hydrocarbon resin is a C-5 hydrocarbon resin having an average of 5 carbon atoms.

6. The adhesive composition of claim 5, wherein the C-5 hydrocarbon resin is produced from one or more monomers selected from the group consisting of cis 1,3 pentadiene, trans 1,3 pentadiene, 2-methyl 2 butene, and cyclopentadienes.

7. The adhesive composition of claim 2, wherein the second hydrocarbon resin is a C-8 to C-10 hydrocarbon resin having an average of 8 to 10 carbon atoms.

8. The adhesive composition of claim 7, wherein the C-8 to C-10 hydrocarbon resin is produced from one or more monomers selected from the group consisting of styrene, vinyl toluene, indene, methyl indene, and alpha methyl styrene.

9. The adhesive composition of claim 1, further comprising 0.1 to 1% by combined weight of one or more fugitive anti-oxidants, freeze-thaw stabilizers, bactericides, and fungicides.

10. The adhesive composition of claim 9, wherein the fugitive anti-oxidant comprises an oxime.

11. The adhesive composition of claim 1, further comprising 20 to 80% by weight of a high solids polymer component with carboxyl functionality.

12. The adhesive composition of claim 11, wherein the high solids polymer component comprises at least one member selected from the group consisting of acrylic, styrene butadiene, ethylene vinyl acetate copolymer, and vinyl acetate ethylene copolymer.

13. The adhesive composition of claim 1, further comprising 0.1 to 1% by weight of a metal naphthanate.

14. The adhesive composition of claim 1, wherein the adhesive is formulated to substantially lack volatile organic compounds that are emitted during curing.

15. The adhesive composition of claim 1, wherein the adhesive has a formulation to cure to have a shear strength of over 5 psi after 15 minutes.

16. The adhesive composition of claim 1, wherein the adhesive has a formulation to cure to have a shear strength of over 200 psi after 3 months.

17. The adhesive composition of claim 1, wherein the adhesive has a formulation to exhibit an open time of up to 60 minutes.

18. A method of building a structure, comprising adhering a first material to a substrate by applying the adhesive of claim 1 between the first material and the substrate and adhering the first material to the substrate.

19. The method of claim 18, wherein the first material is wood flooring.

20. The method of claim 19, wherein the substrate is cement.

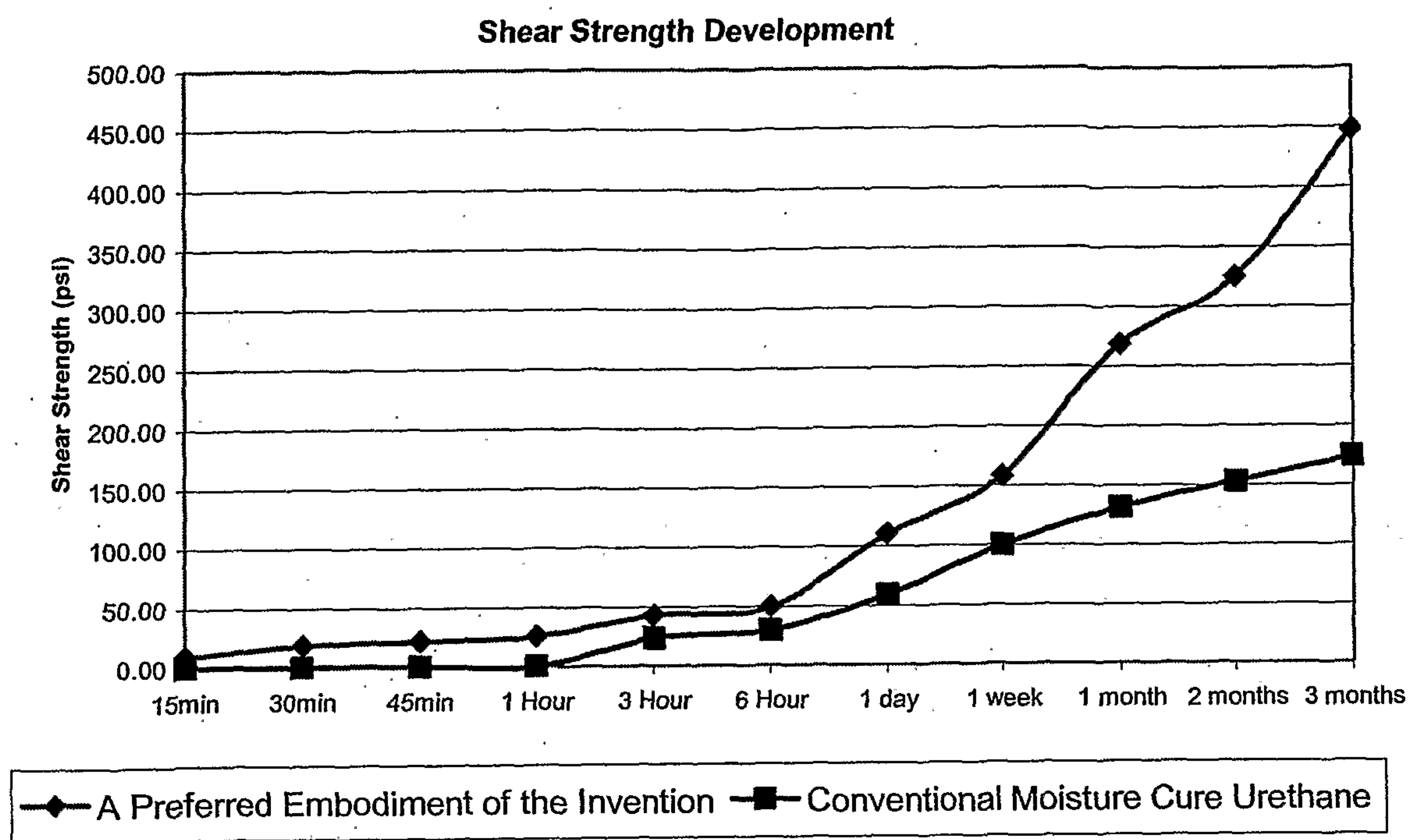
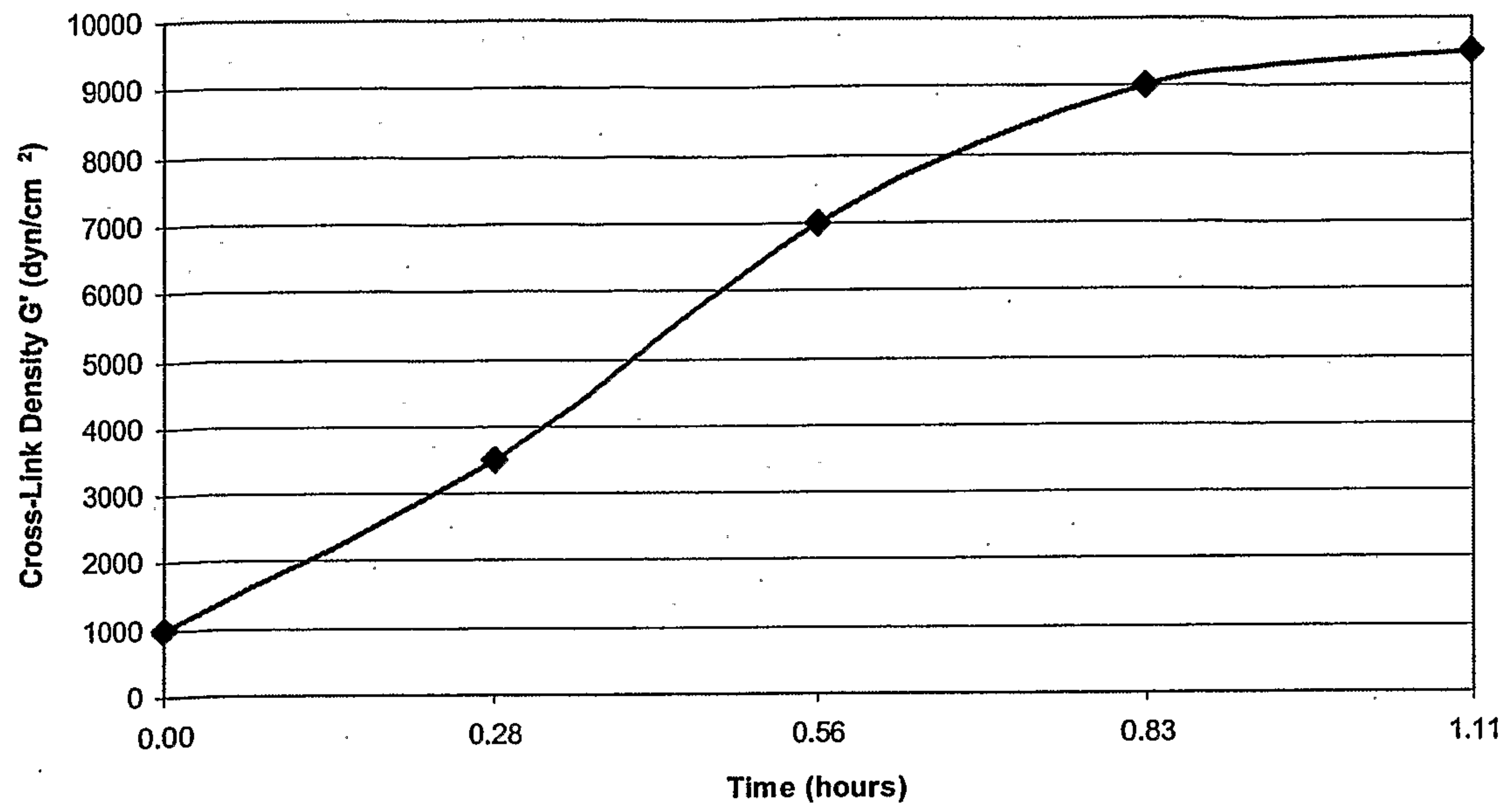
**FIG. 1**

FIG. 2
Cross-link Progression



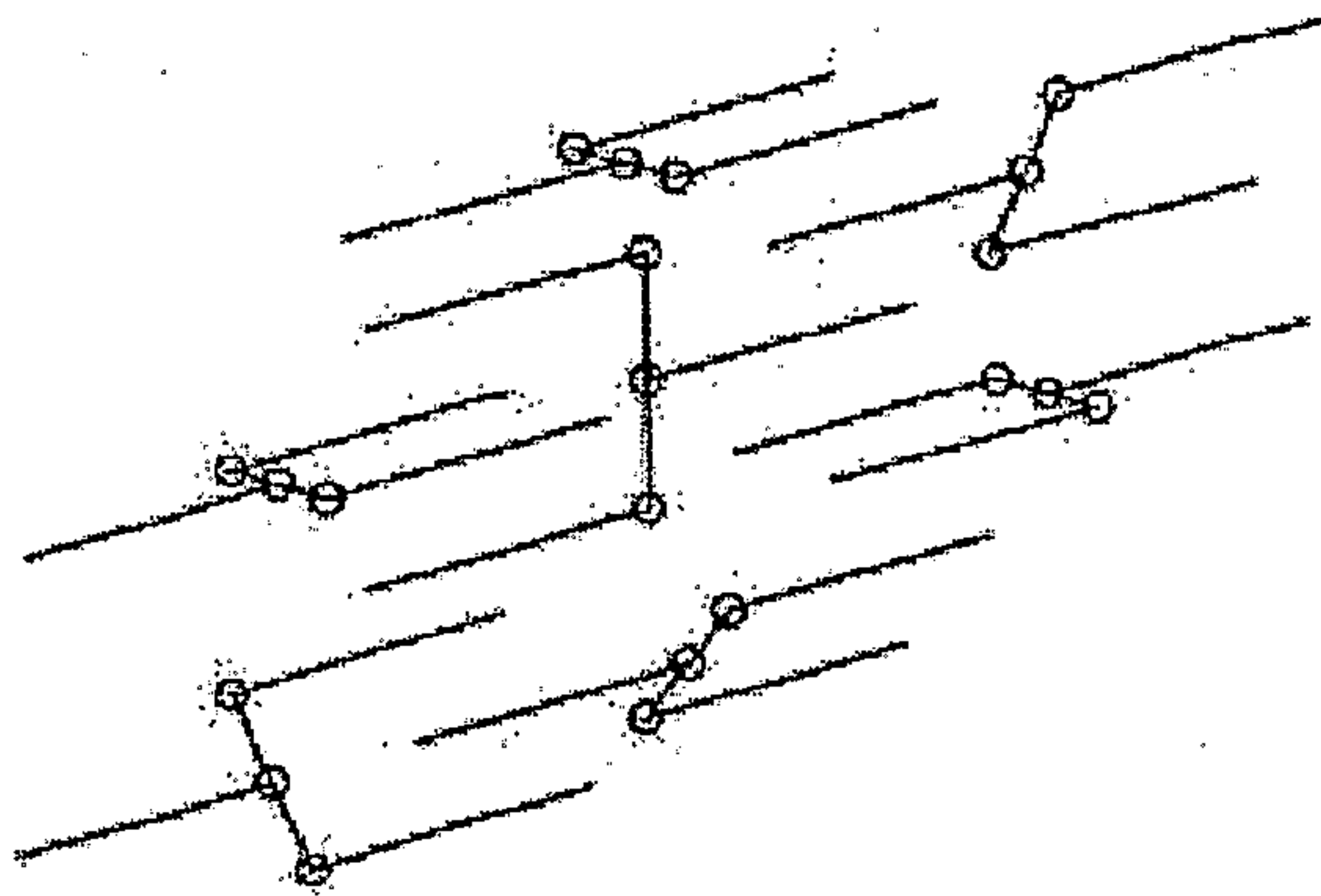


Figure 3

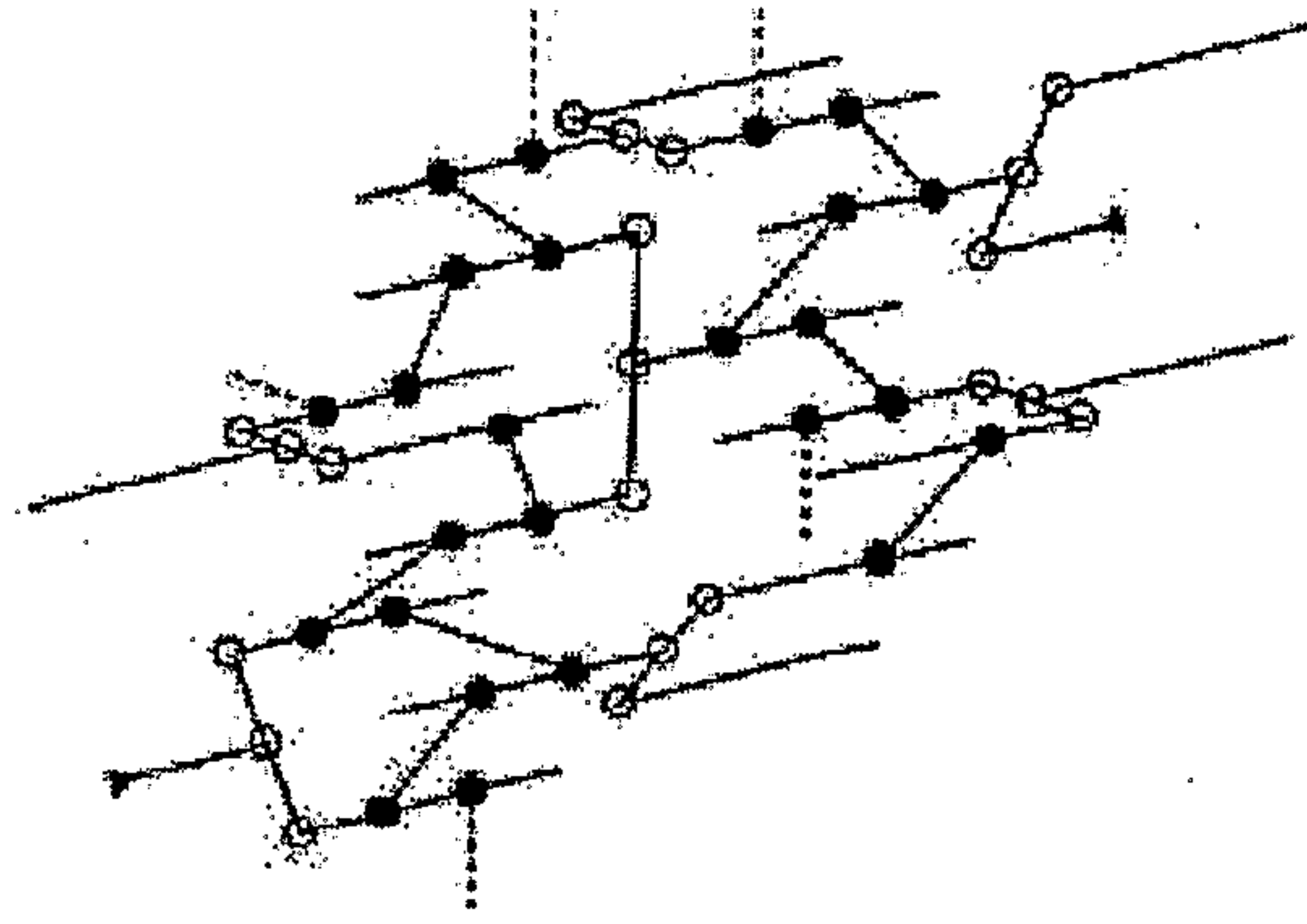


Figure 4

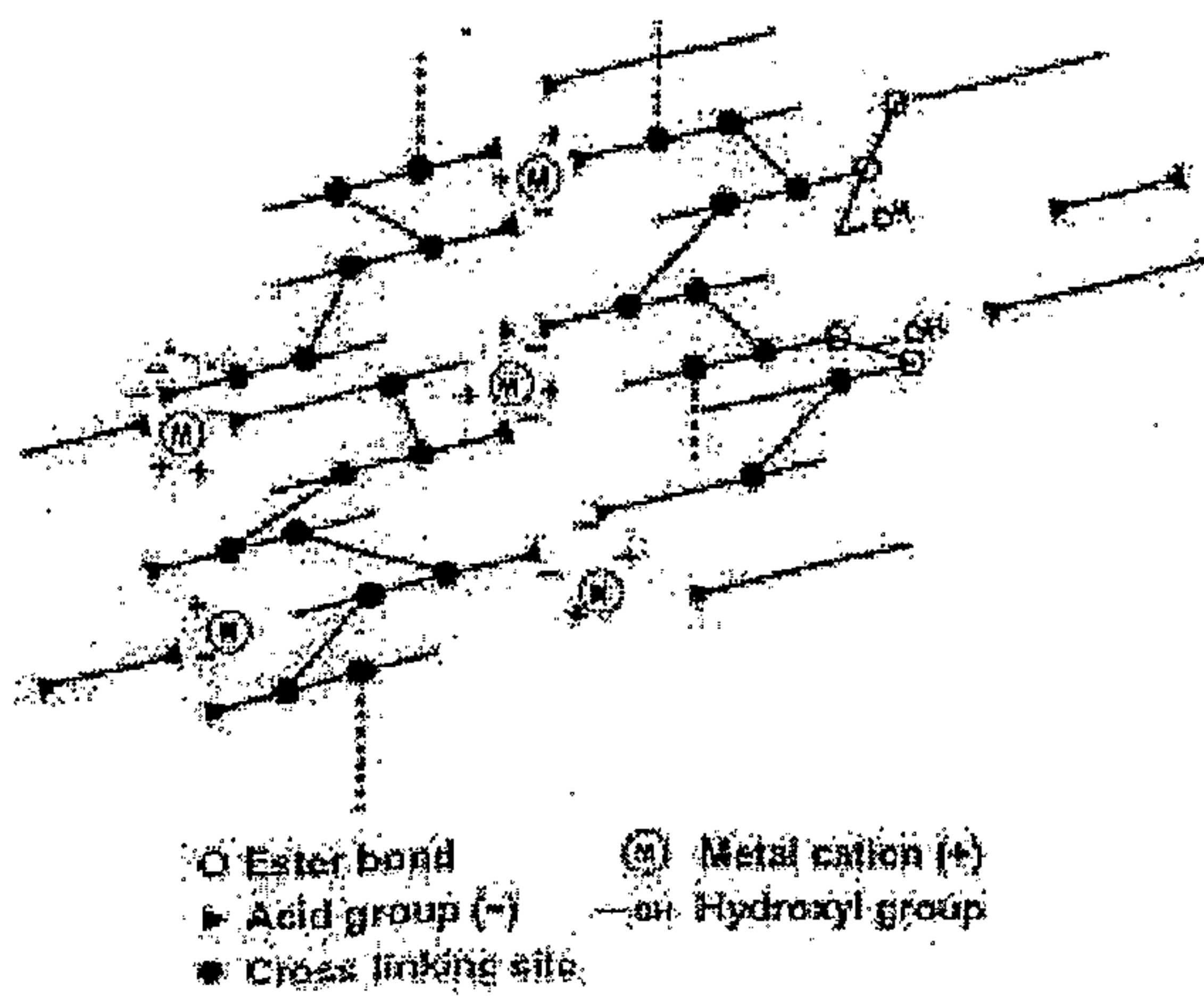
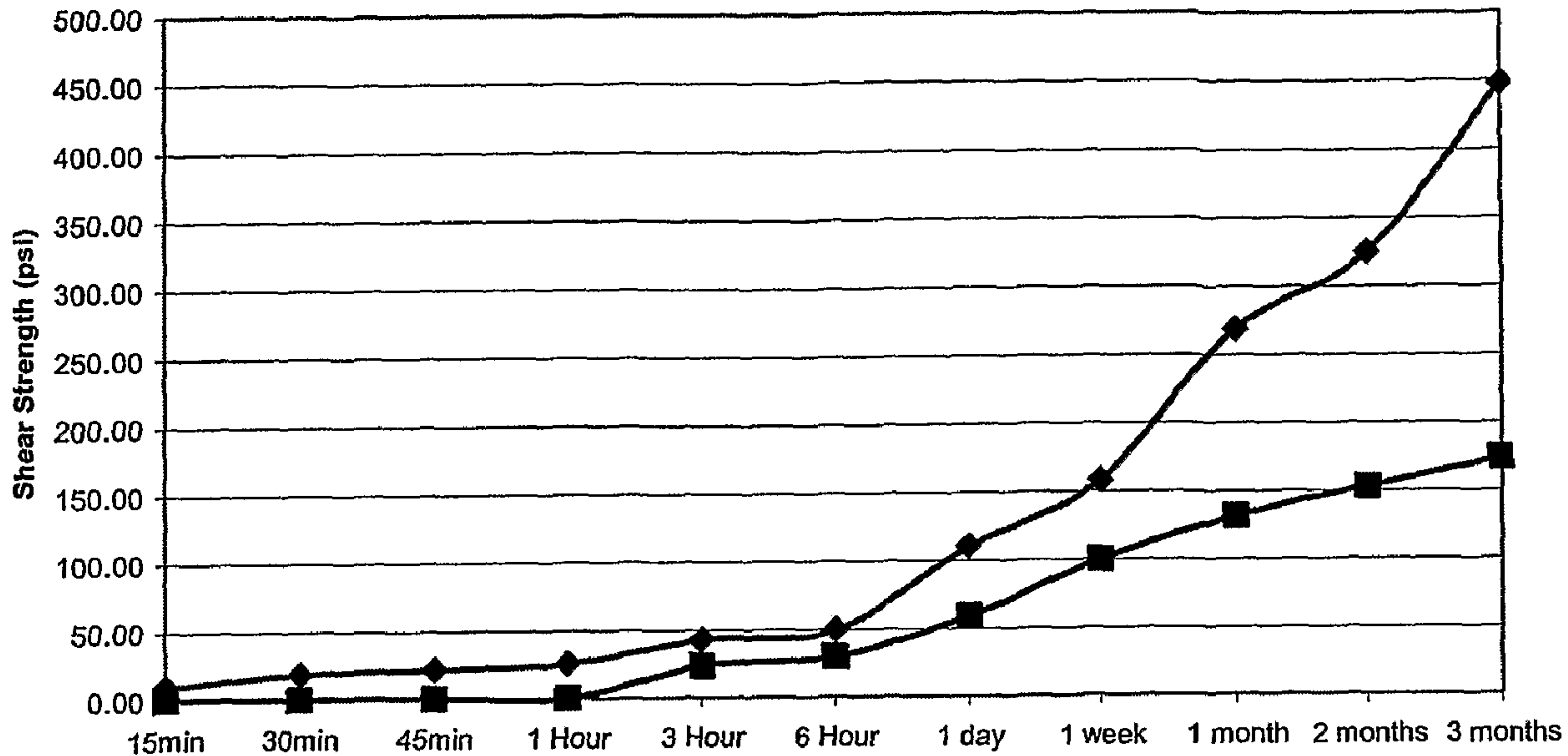


Figure 5

Shear Strength Development



◆ A Preferred Embodiment of the Invention ■ Conventional Moisture Cure Urethane