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(54) **STAIN AND FOULING RESISTANT POLYUREA AND POLYURETHANE COATINGS**

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(57) **ABSTRACT**

Transporters, e.g., ore carriers, vehicles, materials handling equipment, etc. having fluorinated polyurea and fluorinated polyurethane coatings thereon.

STAIN AND FOULING RESISTANT POLYUREA AND POLYURETHANE COATINGS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 60/882,790, filed Dec. 29, 2006.

FIELD

[0002] The present invention relates to polyurea compositions and polyurethane compositions for forming coatings and coatings formed from such compositions. In particular the invention relates to stain and fouling resistant coatings, e.g., for use on rail cars, containers, vehicles, etc.

BACKGROUND

[0003] It has been known to use polyurethane compositions and polyurea compositions for forming coatings on substrates for a variety of purposes. Such compositions have been applied in a variety of approaches including spraying.

[0004] Although such coatings have been used in a variety of applications, a deficiency has been the tendency of such coatings to stain and/or foul. Such staining or fouling may be of mere aesthetic concern or may, in some cases, represent an important functional or performance deficiency.

[0005] A developing energy source is oil from oil sands and tar sands. Such sands tend to stick to equipment and vehicles used to move and process them. As a result, efficiency is reduced as the deposits build up, increasing the weight of moving vehicles, clogging handling chutes, etc. It is common practice today to remove vehicles used in such operations from service for one or two days each week for extensive spray washing to remove the build up of deposits from the vehicle in addition to an extensive solvent wash done on a monthly basis.

[0006] An established energy source is coal which is mined in one location and then shipped to another location via such means as rail car. When removed from the mine, coal commonly contains significant water content and has a temperature of about 40 to about 50° F. (4 to 10° C.). During cool months when the coal is placed in rail cars which are at an ambient temperature close to or below 32° F. (0° C.), the coal will tend to stick to the surfaces of the rail car. When the rail car is emptied significant quantities of the load remain stuck to the car. As a result, as much as 25% of the potential load carrying capacity of the rail cars might be lost. Removal is a labor and cost intensive exercise.

[0007] A need exists for conveniently applied polyurethane compositions and polyurea compositions that provide durable, light weight coatings which exhibit oil-repellency, water-repellency, and stain resistance.

SUMMARY OF INVENTION

[0008] The present invention provides novel polyurethane compositions and polyurea compositions and novel coatings formed therefrom, and transporters, e.g., carriers, vessels, and vehicles, having such coatings thereon.

[0009] In brief summary, the compositions of the invention comprise reactive precursors for forming a polyurethane or polyurea coating and at least one fluorochemical fluorochemical compound.

[0010] The compositions of the invention can be applied in convenient manner, e.g., spraying, to form films or coatings on substrates. The resultant films or coatings can exhibit exceptional physical properties such as high hardness, flexibility, abrasion resistance, and chemical resistance. Durable and light weight, films and coatings of the invention exhibit oil-repellency, water-repellency, and stain resistance. The invention provides polyurethane and polyurea coatings that provide heretofore unattainable resistance to staining and fouling.

DETAILED DESCRIPTION OF INVENTION

[0011] Compositions of the invention comprise reactive precursors for forming polyurethane and/or polyureas and at least one fluorochemical compound. In preferred embodiments, the fluorochemical compound is reactive with one or more of the reactive precursors.

[0012] Polyurethanes can be prepared by reacting one or more isocyanates with one or more polyols. Polyureas can be prepared by reacting one or more isocyanates with one or more amines.

[0013] An illustrative class of fluorochemical compounds suitable for use herein include the fluorochemical monoisocyanates disclosed in U.S. Pat. No. 7,081,545 (Klun et al.) which is incorporated herein by reference in its entirety.

[0014] Fluorochemical alcohols that are useful in carrying out the invention include those represented by the following formula:

$$C_nF_{2n+1}SO_2NCH_3(CH_2)_mOH$$

wherein n=2 to 5, and m=2 to 4 (preferably, n=2 to 4; more preferably, n=4). Fluorochemical alcohols that are useful starting compounds include $C_2F_5SO_2NCH_3(CH_2)_2OH$, $C_2F_5SO_2NCH_3(CH_2)_3OH$, $C_2F_5SO_2NCH_3(CH_2)_4OH$, $C_3F_7SO_2NCH_3(CH_2)_2OH$, $C_3F_7SO_2NCH_3(CH_2)_3OH$, $C_3F_7SO_2NCH_3(CH_2)_4OH$, $C_4F_9SO_2NCH_3(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_3OH$, $C_4F_9SO_2NCH_3(CH_2)_4OH$, $C_5F_{11}SO_2NCH_3(CH_2)_2OH$, $C_5F_{11}SO_2NCH_3(CH_2)_3OH$, $C_5F_{11}SO_2NCH_3(CH_2)_4OH$, and mixtures thereof. Preferred fluorochemical alcohols include, for example, $C_2F_5SO_2NCH_3(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_4OH$, and mixtures thereof. More preferred fluorochemical alcohols include, for example, $C_4F_9SO_2NCH_3(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_4OH$, and mixtures thereof. A most preferred fluorochemical alcohol is $C_4F_9SO_2NCH_3(CH_2)_2OH$. Useful fluorochemical alcohols can be purchased from 3M (St. Paul, Minn.), or can be prepared essentially as described in U.S. Pat. Nos. 2,803,656 (Ahlbrecht et al.) and 6,664,345 (Savu et al.).

[0015] The above-described fluorochemical alcohols can be reacted with 4,4'-diphenylmethane diisocyanate in a solvent to form the corresponding monoisocyanates. 4,4'-Diphenylmethane diisocyanate is commonly known as "methylene diisocyanate" or "MDI". In its pure form, MDI is commercially available as ISONATE™ 125M from the Dow Chemical Company (Midland, Mich.), and as MONDUR™ M from Bayer Polymers (Pittsburgh, Pa.).

[0016] The process of the invention can be carried out with a molar ratio of fluorochemical alcohol:MDI from about 1:1 to about 1:2.5. Preferably, the molar ratio of fluorochemical alcohol:MDI is from about 1:1 to about 1:2. More preferably, the molar ratio is from about 1:1.1 to about 1:1.5.

[0017] The process of the invention can be carried out in a solvent in which the resulting monoisocyanate is not soluble (that is, the solvent is one in which the monoisocyanate partitions out of so that it no longer participates in the reaction). Preferably, the solvent is a nonpolar solvent. More preferably, it is a nonpolar non-aromatic hydrocarbon or halogenated solvent.

[0018] Representative examples of useful solvents include cyclohexane, n-heptane, hexanes, n-hexane, pentane, n-decane, i-octane, octane, methyl nonafluoroisobutyl ether, methyl nonafluorobutyl ether, petroleum ether, and the like, and mixtures thereof. A mixture of methyl nonafluoroisobutyl ether and methyl nonafluorobutyl ether is available as HFE-7100 NOVEC™ Engineered Fluid from 3M. Preferred solvents include, for example, methyl nonafluoroisobutyl ether, methyl nonafluorobutyl ether, petroleum ether, n-heptane, and the like.

[0019] Preferably, the solvent has a Hildebrand solubility parameter (6) of less than about 8.3 $(cal/cm^3)^{1/2}$ (about 17 $MPa^{1/2}$) and a hydrogen bonding index of less than about 4. The Hildebrand solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density (c) of the solvent, which in turn is derived from the heat of vaporization:

$$\delta\bar{c} = \left[\frac{\Delta H - RT}{V_m}\right]^{\frac{1}{2}} \quad (2)$$

[0020] wherein:

[0021] ΔH=heat of vaporization,

[0022] R=gas constant,

[0023] T=temperature, and

[0024] Vm=molar volume

[0025] For example, n-heptane has a Hildebrand solubility index of about 7.4 $(cal/cm^3)^{1/2}$ (about 15 $MPa^{1/2}$), and water has a Hildebrand solubility index of about 23.4 $(cal/cm^3)^{1/2}$ (about 48 $MPa^{1/2}$) (*Principles of Polymer Systems,* 2nd edition, McGraw-Hill Book Company, New York (1982)).

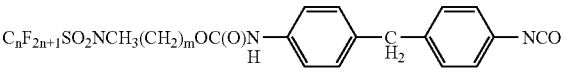
[0026] The hydrogen bonding index is a numerical value that indicates the strength of the hydrogen bonding that occurs in a solvent. Hydrogen bonding values range from −18 to +15. For example, n-heptane has a hydrogen bonding value of about 2.2, and water has a hydrogen bonding value of about 16.2 (*Principles of Polymer Systems,* 2nd edition, McGraw-Hill Book Company, New York (1982)).

[0027] The reaction can be carried out by combining the fluorochemical alcohol and MDI in the solvent. Preferably, the fluorochemical alcohol is added to MDI, which is in the solvent, over time. Optionally, the fluorochemical alcohol can first be dissolved in a solvent such as, for example, toluene, and then added to the MDI in solution. Preferably, the reaction mixture is agitated. The reaction can generally be carried out at a temperature between about 25° C. and about 70° C. (preferably, between about 25° C. and about 50° C.).

[0028] Optionally, the reaction can be carried out in the presence of a catalyst. Useful catalysts include bases (for example, tertiary amines, alkoxides, and carboxylates), metal salts and chelates, organometallic compounds, acids, and urethanes. Preferably, the catalyst is an organotin compound (for example, dibutyltin dilaurate (DBTDL)) or a tertiary amine (for example, diazobicyclo[2.2.2]octane (DABCO)), or a combination thereof. More preferably, the catalyst is DBTDL.

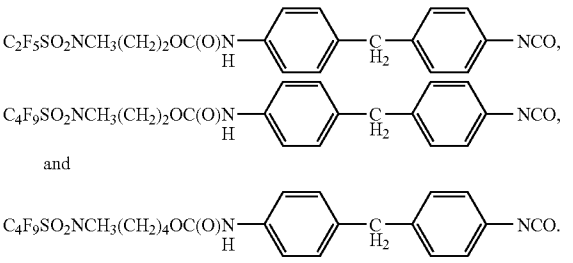
[0029] After the reaction is carried out, the reaction product can be filtered out and dried. The reaction product typically comprises greater than about 85% of the desired fluorochemical monoisocyanate (preferably, greater than about 90%; more preferably, greater than about 95%).

[0030] Fluorochemical monoisocyanates that can be prepared using the process of the invention can be represented by the following formula:



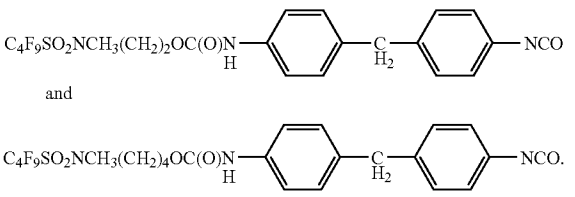
wherein n=2 to 5, and m=2 to 4.

[0031] Preferred fluorochemical monoisocyanates that can be prepared using the process of the invention include, for example:



and

More preferred fluorochemical monoisocyanates prepared using the process of the invention include, for example:



and

[0032] Fluorochemical monoisocyanates prepared using the process of the invention can be useful starting compounds in processes for preparing fluorinated acrylic polymers with water- and oil-repellency properties.

[0033] For example, fluorochemical monoisocyanates prepared using the process of the invention can be reacted with active hydrogen-containing compounds, materials, or surfaces bearing hydroxyl, primary or secondary amines, or thiol groups. The monomer produced by reacting a fluorochemical monoisocyanate prepared by the process of the invention with a hydroxy alkyl acrylate such as hydroxy ethyl acrylate, for

example, can be polymerized (alone or with comonomers) to provide polymers that have useful water- and oil-repellency properties.

[0034] In some preferred embodiments, compositions of the invention will further comprise filler materials such as glass microspheres, glass bubbles, ceramic microspheres, or other particles.

[0035] The surprising combination of properties exhibited by films and coatings of the invention makes them advantageously suited for a variety of applications.

[0036] For example, coatings of the invention can be used as coatings on motor vehicle bodies, undercarriages, truck beds, carriers and vessels used for transporting materials, etc. The coatings exhibit good adhesion to metal substrates coupled with oil-repellency, water-repellency, and stain resistance.

[0037] An illustrative application of the compositions and coatings of the invention is on equipment and vehicles used in mining operations, e.g., for oil sands and tar sands. Despite the tendency of such sands to stick to equipment and vehicles used to move and process them, use of coatings of the invention will reduce the maintenance time required to clean conventional equipment and vehicles, thereby reducing down-time and increasing efficiency of operations. With the improved release properties achieved in accordance with the present invention, such costly down-time operations can be reduced, resulting in greater productivity, lower operating costs, etc. Similarly, railcars can outfitted with coatings of the invention to reduce the build up of coal, resulting in increased transportation efficiency.

[0038] The invention may be used to advantageous effect in a variety of applications where durable, abrasion-resistant coatings exhibiting oil-repellency, water-repellency, and stain resistance and desired.

[0039] Coatings of the invention exhibit good adhesion to metal substrates.

[0040] Coatings of the invention preferably contain glass microspheres and or bubbles to impart improved insulative properties (e.g., thermal insulation, noise dampening, vibration, etc.), reduce effective weight of the coating. In some embodiments, coatings of the invention are made in combination with open celled, foamed construction.

[0041] Coatings of invention can be made with superior abrasion resistance and hardness.

[0042] Compositions of invention can be applied by any of a variety of techniques. In some embodiments, compositions of the invention can be applied by such convenient techniques as spraying.

[0043] Coatings of the invention can applied over other, less durable insulation materials to provide optimized, composite properties. For example, the present invention may be used to provide a polyurea insulation coating sprayed over other insulation materials such as polystyrene or polyurethane open cell foam insulation, or other insulative material.

[0044] Films and coatings of the invention may be used in conjunction with other materials and layers to make multi-layer composite constructions offering desired performance. For example, Compositions of the invention can be coated over blast and tear resistant films to impart improved blast and/or projectile resistance.

[0045] The combination of convenient application and high performance provided by compositions and coatings of the invention makes them well suited for a wide variety of applications. Some examples include protective coatings to protect the cab, passenger compartment, load area, or other chambers of vehicles including aircraft, watercraft and land vehicles. For example, the invention provides advantageous results on wheeled and tracked vehicles, e.g., trucks, HUMVEEs, tanks, etc., airplanes, space vehicles, helicopters, boats and other enclosed cockpit vehicles, from heat from engines or ambient sources. Other examples include protective coatings on equipment and vehicles or vehicle components that are used in extreme environments, e.g., trucks, tanks, airplanes, space vehicles, helicopters, boats, pipes, bridges, off-shore oil platforms, and other metallic substrates used in extreme environments or washed with bleach and other corrosive materials to provide corrosion resistance for the metal substrates. The invention can be used on a variety of materials handling equipment including wheelbarrows, pipelines, sluices, etc.

EXAMPLES

[0046] The invention will be further explained with the following illustrative examples.

Test Methods

[0047] Dynamic Contact Angle Measurement

[0048] Advancing and receding contact angles on the polyurea samples were measured using a CAHN Dynamic Contact Angle Analyzer, Model DCA 322 (a Wilhelmy balance apparatus equipped with a computer for control and data processing, commercially available from ATI, Madison, Wis.). Water was used as the probe liquid.

[0049] Static Contact Angle Measurement

[0050] The treated substrates were tested for their contact angles versus water using an Olympus TGHM goniometer (Olympus Corp, Pompano Beach, Fla.). Contact angles were measured at least 24 hrs after cure. The values are the mean values of 4 measurements and are reported in degrees. The minimum measurable value for a contact angle was 20. A value less than 20 means that the liquid spreads on the surface.

[0051] Thermal Conductivity Test Method 1

[0052] Thermal conductivity was measured using a Model 2021 Thermal Conductivity Apparatus (available from Anter Corporation, Pittsburgh, Pa.) following ASTM E 1530 (Test Method for Evaluating the Resistance to Thermal Transmission of Thin Specimens of Materials by the Guarded Flow Meter Technique).

[0053] Thermal Conductivity Test Method 2—Hot Face vs. Cold Face

[0054] A 4 inch×6 inch (10.16 cm×15.24 cm) rectangular hole was cut in the top of a lab furnace (Econo-Kiln, Model K 14, L & L Manufacturing Co., Twin Oaks, Pa.; maximum temperature of 1832° F. (1000° C.)). The sample to be tested was placed over the rectangular hole in the furnace such that the edges of the sample fully overlapped on all sides of the opening. Two thermocouples (Type K Thermocouple Thermometer, Model 650, Omega Engineering, Inc., Stamford, Conn.) were placed in the center of the sample and held in contact with a foil tape. One thermocouple measures the external face temperature ($T_{Outside}$) of the sample (that portion outside the oven) and one thermocouple measures the internal face temperature T_{Inside} of the sample (that portion inside the furnace). The furnace oven was turned on and the

I_{Inside} of the sample was adjusted to 200° F. (93.3° C.). After several minutes, the $T_{Outside}$ was recorded. Additionally, Model ThermaCAM™ P65 infrared camera, available from Flir Systems Inc., Portland, Oreg., was used to analyze the temperature of the external face surface of the sample.

Comparative Example 1

[0055] A two component polyurea (Part A and Part B) was formulated as follows. Part A contained hexamethylene diisocyanate (85.2% by weight, obtained from Rhodia, Inc., Cranbury, N.J., under the trade designation "TOLONATE™ HDT LV2"), glass microspheres (13.5% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37") and a modified polyurea (1.3% by weight, obtained from BYK Chemie, Wesel, Germany, under the trade designation "BYK™ 410"). Part B contained diethyltoluenediamine (32.4% by weight, obtained from Albemarle Corporation, Bayport, Tex., under the trade designation "ETHACURE™ 100"), polyoxypropylenediamine (39.6% by weight, obtained from Huntsman Corporation, Salt Lake City, Utah under the trade designation "JEFFAMINE™ D-2000"), an aromatic secondary diamine (6.5% by weight, obtained from UOP, A Honeywell Company, Tonawanda, N.Y., under the trade designation "UNILINK™ 4200"), a trifunctional amine (2.4% by weight, obtained from Huntsman Corporation under the trade designation "JEFFAMINE™ T-5000"), glass microspheres (18.2% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (0.8% by weight, obtained from BYK Chemie, under the trade designation "BYK™ 410") and a liquid organic pigment to produce the desired color (0.1%).

[0056] Parts A and B were sprayed from a plural component proportioning sprayer (obtained from Graco, Minneapolis, Minn., under the trade designation "REACTOR H-XP2" using a "FUSION MP" spray gun with nozzles. Each part (A and B) was kept separate until they exited the spray gun. The two components, A and B, were stirred, in separate pots, in the spray unit and maintained at a temperature of 160° F. (71° C.) during the spray process. The materials (Parts A and B) were sprayed on to a cold roll steel panel that was previously sprayed with a release agent (from Sierra Paint Co., Minnetonka, Minn., under the trade designation "TK-709 UR") and also waxed paper. The formulation cured within about 20 seconds. After a period of time the sprayed panels were peeled from the metal substrate and waxed paper and tested as described above. The contact angle data is listed in Table 1. Thermal conductivity data is listed in Table 2.

Example 1

[0057] A two component polyurea (Part A and Part B) was formulated as follows. Part A contained hexamethylene diisocyanate (85.2% by weight, obtained from Rhodia, Inc., Cranbury, N.J., under the trade designation "TOLONATE™ HDT LV2"), glass microspheres (13.5% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37") and a modified polyurea (1.3% by weight, obtained from BYK Chemie, Wesel, Germany, under the trade designation "BYK™ 410"). Part B contained diethyltoluenediamine (31.6% by weight, obtained from Albemarle Corporation, Bayport, Tex., under the trade designation "ETHACURE 100"), polyoxypropylenediamine (38.7% by weight, obtained from Huntsman Corporation, Salt Lake City, Utah, under the trade designation "JEFFAMINE™ D-2000"), an aromatic secondary diamine (6.3% by weight, obtained from UOP, A Honeywell Company, Tonawanda, N.Y. under the trade designation "UNILINK™ 4200"), a trifunctional amine (2.4% by weight, obtained from Huntsman Corporation under the trade designation "JEFFAMINE™ T-5000"), glass microspheres (17.8% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (0.7% by weight, obtained from BYK Chemie, under the trade designation "BYK™ 410"), deionized water (2.4% by weight) and a liquid organic pigment to produce the desired color (0.1%).

[0058] Parts A and B were sprayed from a plural component proportioning sprayer (obtained from Graco, Minneapolis, Minn., under the trade designation "REACTOR H-XP2" using a "FUSION MP" spray gun with nozzles. Each part (A and B) was kept separate until they exited the spray gun. The two components, A and B, were stirred, in separate pots, in the spray unit and maintained at a temperature of 160° F. (71° C.) during the spray process. The materials (Parts A and B) were sprayed on to a cold roll steel panel that was previously sprayed with a release agent (from Sierra Paint Co., Minnetonka, Minn., under the trade designation "TK-709 UR") and also waxed paper. The formulation cured within about 20 seconds. After a period of time the sprayed panels were peeled from the metal substrate and waxed paper. The contact angle data is listed in Table 1. Thermal conductivity data is listed in Table 2.

Example 2

[0059] A two component polyurea (Part A and Part B) was formulated as follows. Part A contained hexamethylene diisocyanate (84.4% by weight, obtained from Rhodia, Inc., Cranbury, N.J., under the trade designation "TOLONATE™ HDT LV2"), glass microspheres (12.3% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (1.3% by weight, obtained from BYK Chemie, Wesel, Germany, under the trade designation "BYK™ 410") and a fluorochemical urethane (2% by weight, obtained from 3M Company under the trade designation "SRC-220". Part B contained diethyltoluenediamine (32.4% by weight, obtained from Albemarle Corporation, Bayport, Tex., under the trade designation "ETHACURE™ 100"), polyoxypropylenediamine (39.6% by weight, obtained from Huntsman Corporation, Salt Lake City, Utah under the trade designation "JEFFAMINE™ D-2000"), an aromatic secondary diamine (6.5% by weight, obtained from UOP, A Honeywell Company, Tonawanda, N.Y. under the trade designation "UNILINK™ 4200"), a trifunctional amine (2.4% by weight, obtained from Huntsman Corporation under the trade designation "JEFFAMINE™ T-5000"), glass microspheres (18.2% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (0.8% by weight, obtained from BYK Chemie, under the trade designation "BYK™ 410"), and a liquid organic pigment to produce the desired color (0.1%).

[0060] Parts A and B were sprayed from a plural component proportioning sprayer (obtained from Graco, Minneapolis, Minn., under the trade designation "REACTOR H-XP2" using a "FUSION MP" spray gun with nozzles. Each part (A and B) was kept separate until they exited the spray gun. The two components, A and B, were stirred, in separate pots, in the spray unit and maintained at a temperature of 160° F. (71° C.) during the spray process. The materials (Parts A and B) were sprayed on to a cold roll steel panel that was previously sprayed with a release agent (from Sierra Paint Co., Minnetonka, Minn., under the trade designation "TK-709 UR")

and also waxed paper. The formulation cured within about 20 seconds. After a period of time the sprayed panels were peeled from the metal substrate and waxed paper and tested as described above. The data is listed in Table 1.

Example 3

[0061] A two component polyurea (Part A and Part B) was formulated as follows. Part A contained hexamethylene diisocyanate (76.8% by weight, obtained from Rhodia, Inc., Cranbury, N.J., under the trade designation "TOLONATE™ HDT LV2"), glass microspheres (12.2% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (1.0% by weight, obtained from BYK Chemie, Wesel, Germany, under the trade designation "BYK 410") and a fluorochemical urethane (10% by weight, obtained from 3M Company under the trade designation "SRC-220". Part B contained diethyltoluenediamine (32.4% by weight, obtained from Albemarle Corporation, Bayport, Tex., under the trade designation "ETHACURE™ 100"), polyoxypropylenediamine (39.6% by weight, obtained from Huntsman Corporation, Salt Lake City, Utah under the trade designation "JEFFAMINE™ D-2000"), an aromatic secondary diamine (6.5% by weight, obtained from UOP, A Honeywell Company, Tonawanda, N.Y., under the trade designation "UNILINK™ 4200"), a trifunctional amine (2.4% by weight, obtained from Huntsman Corporation under the trade designation "JEFFAMINE™ T-5000"), glass microspheres (18.2% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (0.8% by weight, obtained from BYK Chemie, under the trade designation "BYK™ 410"), and a liquid organic pigment to produce the desired color (0.1%).

[0062] Parts A and B were sprayed from a plural component proportioning sprayer (obtained from Graco, Minneapolis, Minn., under the trade designation "REACTOR H-XP2" using a "FUSION MP" spray gun with nozzles. Each part (A and B) was kept separate until they exited the spray gun. The two components, A and B, were stirred, in separate pots, in the spray unit and maintained at a temperature of 160° F. (71° C.) during the spray process. The materials (Parts A and B) were sprayed on to a cold roll steel panel that was previously sprayed with a release agent (from Sierra Paint Co., Minnetonka, Minn., under the trade designation "TK-709 UR") and also waxed paper. The formulation cured within about 20 seconds. After a period of time the sprayed panels were peeled from the metal substrate and waxed paper and tested as described above. The data is listed in Table 1.

Example 4

[0063] A two component polyurea (Part A and Part B) was formulated as follows. Part A contained hexamethylene diisocyanate (81.8% by weight, obtained from Rhodia, Inc., Cranbury, N.J., under the trade designation "TOLONATE™ HDT LV2"), glass microspheres (13.0% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (1.2% by weight, obtained from BYK Chemie, Wesel, Germany, under the trade designation "BYK™ 410") and a fluorochemical monoisocyanate (4% by weight, as prepared in U.S. Pat. No. 7,081,545 (Klun et al.) Example 5, which is incorporated by reference to the extent that it is not inconsistent with the present disclosure). Part B contained diethyltoluenediamine (32.4% by weight, obtained from Albemarle Corporation, Bayport, Tex., under the trade designation "ETHACURE™ 100"), polyoxypropylenediamine (39.6% by weight, obtained from Huntsman Corporation, Salt Lake City, Utah under the trade designation "JEFFAMINE™ D-2000"), an aromatic secondary diamine (6.5% by weight, obtained from UOP, A Honeywell Company, Tonawanda, N.Y., under the trade designation "UNILINK™ 4200"), a trifunctional amine (2.4% by weight, obtained from Huntsman Corporation under the trade designation "JEFFAMINE™ T-5000"), glass microspheres (18.2% by weight, obtained from 3M Company under the trade designation "3M™ GLASS MICROSPHERES K37"), a modified polyurea (0.8% by weight, obtained from BYK Chemie, under the trade designation "BYK™ 410"), and a liquid organic pigment to produce the desired color (0.1%).

[0064] Parts A and B were sprayed from a plural component proportioning sprayer (obtained from Graco, Minneapolis, Minn., under the trade designation "REACTOR H-XP2" using a "FUSION MP" spray gun with nozzles. Each part (A and B) was kept separate until they exited the spray gun. The two components, A and B, were stirred, in separate pots, in the spray unit and maintained at a temperature of 160° F. (71° C.) during the spray process. The materials (Parts A and B) were sprayed on to a cold roll steel panel that was previously sprayed with a release agent (from Sierra Paint Co., Minnetonka, Minn., under the trade designation "TK-709 UR") and also waxed paper. The formulation cured within about 20 seconds. After a period of time the sprayed panels were peeled from the metal substrate and waxed paper and tested as described above. The data is listed in Table 1.

TABLE 1

	Static Contact Angle H2O		Dynamic Advancing Contact Angle (H_2O)		Dynamic Receding Contact Angle (H_2O)	
	Sprayed On Steel	Sprayed On Waxed Paper	Sprayed On Steel	Sprayed On Waxed Paper	Sprayed On Steel	Sprayed On Waxed Paper
Comparative Example 1	73.1	65	78.2	72.2	42.5	45.6
Example 2	76.8	65.8	77.9	77.4	48.0	46.8
Example 3	91.2	97.9	99	100	33.1	32
Example 4	90	81.5	79.5	74.8	58.0	49.3

[0065]

TABLE 2

Test Method	Comparative Example 1	Example 1
Thermal Conductivity Test Method 2-Hot Face vs. Cold Face	250° F./115° F.	250° F./104° F.
Thermal Conductivity Test Method 1	K = 0.1 W/mK @ 58° C.	K = 0.07 W/mK @ 58° C.

[0066] Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

What is claimed is:

1. A transporter having a coating on at least a portion of the surface thereof, said coating selected from the group consisting of polyureas, polyurethanes, and combinations thereon which are the reaction products of precursors including at least one fluorochemical compound.

2. The transporter of claim 1 wherein said transporter is selected from the group consisting of rail cars, trucks, automobiles, wheelbarrows, carts, carriers, conveyor belts, tanks, tankers, aircraft, watercraft, pipelines, and sluices.

3. The transporter of claim 1 wherein said fluorochemical compounds is a fluorinated isocyanate.

4. The transporter of claim 3 wherein said fluorinated isocyanate is a fluorinated monoisocyanate.

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