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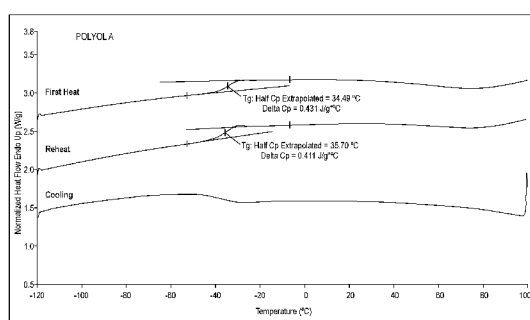


FIG. 1

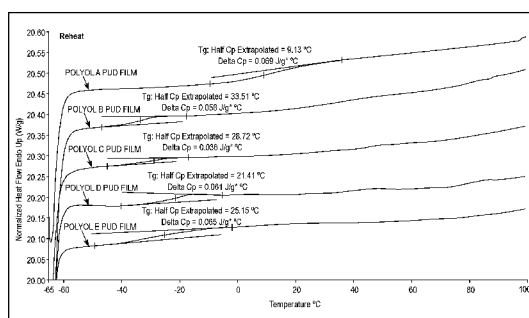


FIG. 7

(57) Abstract: The present invention provides an aqueous polyurethane dispersion (PUD) comprising an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry of less than -30°C ; wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%. Coatings, adhesives and sealants made from the inventive aqueous polyurethane dispersion (PUD) pass detergent resistance testing according to the American Architectural Manufacturers Association's standard, AAMA 615-13, have a pencil hardness according to ASTM D3363 of at least 3H, and are particularly suited for use on low surface energy substrates such as vinyl surfaces including floors, windows, doors, window frames, door frames, window shutters, railing, gates, pillars, arbors, pergolas, trellises, gazebos, posts, fencing, pipes and fittings, wire and cable insulation, automobile components, credit cards, and siding.

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ONE COMPONENT POLYURETHANE DISPERSION FOR VINYL WINDOWS

FIELD OF THE INVENTION

[0001] The present invention relates in general to polymers and, more specifically, to one component polyurethane dispersions which adhere well to vinyl substrates.

BACKGROUND OF THE INVENTION

[0002] As those skilled in the art are aware, it has proven very difficult to develop coatings which will adhere well to vinyl windows. This is because vinyl typically contains plasticizers such as dialkyl phthalates, alkyl aryl phosphates, alkyl aryl phthalates, aryl phosphates, etc., which interfere with the ability of the coating to adhere to the substrate.

[0003] In addition to the chemistry-related problems of trying to adhere a coating to vinyl, the American Architectural Manufacturers Association (AAMA) has very stringent standards for window coatings, including those for vinyl windows regarding a variety of parameters such as chemical resistance, detergent resistance, humidity resistance and pencil hardness.

[0004] To reduce or eliminate problems with adhering coatings to vinyl substrates such as windows, therefore, a need exists in the art for a coating which will adhere to vinyl but still provide the necessary chemical, detergent, and humidity resistances and pencil hardness to permit the use in vinyl window coatings.

SUMMARY OF THE INVENTION

[0005] Accordingly, the present invention addresses problems inherent in the art by providing a durable, chemically-resistant coating that can be applied as a one-component, low VOC system.

[0006] The present invention provides a one-component polyurethane dispersion (PUD) based on ortho-phthalic based polyester polyols with a range of molecular weights. This chemistry provides coatings, adhesives

and sealants having excellent chemical resistance, especially with regard to aggressive detergent testing. In addition, this invention provides coatings, adhesives and sealants with augmented adhesion to low-surface energy substrates and improved hardness, while retaining low (or no) volatile organic content. The instant invention provides two-component performance with a one-component coating.

[0007] These and other advantages and benefits of the present invention will be apparent from the Detailed Description of the Invention herein below.

BRIEF DESCRIPTION OF THE FIGURES

[0008] The present invention will now be described for purposes of illustration and not limitation in conjunction with the figures, wherein:

[0009] FIG. 1 is a differential scanning calorimetry (DSC) thermogram of POLYOL A;

[0010] FIG. 2 is a differential scanning calorimetry (DSC) thermogram of POLYOL B;

[0011] FIG. 3 is a differential scanning calorimetry (DSC) thermogram of POLYOL C;

[0012] FIG. 4 is a differential scanning calorimetry (DSC) thermogram of POLYOL E:

[0013] FIG. 5 is a differential scanning calorimetry (DSC) thermogram of POLYOL D;

[0014] FIG. 6 is a differential scanning calorimetry (DSC) thermogram of the first heat of films made from the same polyurethane dispersion (PUD) and containing one of POLYOLS A, B, C, D, and E; and

[0015] FIG. 7 is a differential scanning calorimetry (DSC) thermogram of the reheat of films made from the same polyurethane dispersion (PUD) and containing one of POLYOLS A, B, C, D, and E.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The present invention will now be described for purposes of illustration and not limitation. Except in the operating examples, or where otherwise indicated, all numbers expressing quantities, percentages, and so forth in the specification are to be understood as being modified in all instances by the term “about.”

[0017] Any numerical range recited in this specification is intended to include all sub-ranges of the same numerical precision subsumed within the recited range. For example, a range of “1.0 to 10.0” is intended to include all sub-ranges between (and including) the recited minimum value of 1.0 and the recited maximum value of 10.0, that is, having a minimum value equal to or greater than 1.0 and a maximum value equal to or less than 10.0, such as, for example, 2.4 to 7.6. Any maximum numerical limitation recited in this specification is intended to include all lower numerical limitations subsumed therein and any minimum numerical limitation recited in this specification is intended to include all higher numerical limitations subsumed therein. Accordingly, Applicants reserve the right to amend this specification, including the claims, to expressly recite any sub-range subsumed within the ranges expressly recited herein. All such ranges are intended to be inherently described in this specification such that amending to expressly recite any such sub-ranges would comply with the requirements of 35 U.S.C. §112(a), and 35 U.S.C. §132(a).

[0018] Any patent, publication, or other disclosure material identified herein is incorporated by reference into this specification in its entirety unless otherwise indicated, but only to the extent that the incorporated material does not conflict with existing definitions, statements, or other disclosure material expressly set forth in this specification. As such, and to the extent necessary, the express disclosure as set forth in this specification supersedes any conflicting material incorporated by reference herein. Any material, or portion thereof, that is said to be incorporated by reference into this specification, but which conflicts with existing

definitions, statements, or other disclosure material set forth herein, is only incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material. Applicants reserve the right to amend this specification to expressly recite any subject matter, or portion thereof, incorporated by reference herein.

[0019] Reference throughout this specification to “various non-limiting embodiments,” “certain embodiments,” or the like, means that a particular feature or characteristic may be included in an embodiment. Thus, use of the phrase “in various non-limiting embodiments,” “in certain embodiments,” or the like, in this specification does not necessarily refer to a common embodiment, and may refer to different embodiments. Further, the particular features or characteristics may be combined in any suitable manner in one or more embodiments. Thus, the particular features or characteristics illustrated or described in connection with various or certain embodiments may be combined, in whole or in part, with the features or characteristics of one or more other embodiments without limitation. Such modifications and variations are intended to be included within the scope of the present specification. The various embodiments disclosed and described in this specification can comprise, consist of, or consist essentially of the features and characteristics as variously described herein.

[0020] The grammatical articles “a”, “an”, and “the”, as used herein, are intended to include “at least one” or “one or more”, unless otherwise indicated, even if “at least one” or “one or more” is expressly used in certain instances. Thus, these articles are used in this specification to refer to one or more than one (i.e., to “at least one”) of the grammatical objects of the article. By way of example, and without limitation, “a component” means one or more components, and thus, possibly, more than one component is contemplated and may be employed or used in an implementation of the described embodiments. Further, the use of a

singular noun includes the plural, and the use of a plural noun includes the singular, unless the context of the usage requires otherwise.

[0021] In various non-limiting embodiments, the present invention provides an aqueous polyurethane dispersion (PUD) comprising an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C ; wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry of 0°C to 20°C and a hard block content of greater than 50 %.

[0022] Coatings made from the inventive aqueous polyurethane dispersion (PUD) pass detergent resistance testing according to the American Architectural Manufacturers Association's standard, AAMA 615-13, with a minimum 90% gloss retention, maximum color change of 5 delta E, no blistering and no loss of adhesion after testing, exhibits no staining by betadine after four hours, and pass humidity resistance testing according to ASTM D714 with no blistering. The inventive polyurethane dispersions are particularly well suited for use in or as coatings adhesives, sealants, and paints applied to vinyl substrates, including but not limited to, floors, windows, doors, window frames, window surrounds, door frames, window shutters, railing, gates, pillars, arbors, pergolas, trellises, gazebos, posts, fencing, pipes and fittings, wire and cable insulation, automobile components, credit cards, cladding and siding.

[0023] The present inventors have surprisingly found that coatings, adhesives, sealants, and paints produced from the inventive polyurethane dispersions have excellent chemical resistance properties, especially with regard to aggressive detergent testing. In addition, these dispersions provide coatings, adhesives, sealants, and paints with augmented adhesion to low-surface energy substrates and improved hardness properties, while retaining low (or no) volatile organic content.

[0024] As used herein, “polymer” encompasses prepolymers, oligomers and both homopolymers and copolymers; the prefix “poly” in this context referring to two or more. As used herein, “molecular weight”, when used in reference to a polymer, refers to the number average molecular weight (“ M_n ”), unless otherwise specified. As used herein, the M_n of a polymer containing functional groups, such as a polyol, can be calculated from the functional group number, such as hydroxyl number, which is determined by end-group analysis.

[0025] As used herein, “soft blocks” contain polyethers, polyesters and polycarbonates and “hard blocks” contain urethanes, urea groups, short chain amines, diols and diisocyanates. In some embodiments, the inventive compositions have a hard block content of greater than 50%. In certain other embodiments, the inventive compositions have a hard block content of 50% to 60%. In various embodiments, the inventive compositions have a hard block content of 55% to 60%.

[0026] As used herein, the term “aliphatic” refers to organic compounds characterized by substituted or un-substituted straight, branched, and/or cyclic chain arrangements of constituent carbon atoms. Aliphatic compounds do not contain aromatic rings as part of the molecular structure thereof. As used herein, the term “cycloaliphatic” refers to organic compounds characterized by arrangement of carbon atoms in closed ring structures. Cycloaliphatic compounds do not contain aromatic rings as part of the molecular structure thereof. Therefore, cycloaliphatic compounds are a subset of aliphatic compounds. Therefore, the term “aliphatic” encompasses aliphatic compounds and cycloaliphatic compounds.

[0027] As used herein, “diisocyanate” refers to a compound containing two isocyanate groups. As used herein, “polyisocyanate” refers to a compound containing two or more isocyanate groups. Hence, diisocyanates are a subset of polyisocyanates.

[0028] As used herein, the term "dispersion" refers to a composition comprising a discontinuous phase distributed throughout a continuous phase. For example, "waterborne dispersion" and "aqueous dispersion" refer to compositions comprising particles or solutes distributed throughout liquid water. Waterborne dispersions and aqueous dispersions may also include one or more co-solvents in addition to the particles or solutes and water. As used herein, the term "dispersion" includes, for example, colloids, emulsions, suspensions, sols, solutions (i.e., molecular or ionic dispersions), and the like.

[0029] As used herein, the term "aqueous polyurethane dispersion" means a dispersion of polyurethane particles in a continuous phase comprising water. As used herein, the term "polyurethane" refers to any polymer or oligomer comprising urethane (i.e., carbamate) groups, urea groups, or both. Thus, the term "polyurethane" as used herein refers collectively to polyurethanes, polyureas, and polymers containing both urethane and urea groups, unless otherwise indicated.

[0030] In certain embodiments, the aqueous polyurethane dispersion (PUD) that is used in the present invention comprises one or more polyurethanes that are the reaction product of reactants comprising, consisting essentially of, or, in some cases, consisting of: a polyisocyanate; a polymeric polyol having a number average molecular weight ("M_n") of 400 to 8,000 g/mol; and a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group.

[0031] The present invention is directed to an aqueous polyurethane dispersion (PUD) comprising the reaction product of: (i) a polyisocyanate; (ii) a polymeric polyol having a number average molecular weight of 400 to 8000 g/mol; (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group; (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by

differential scanning calorimetry (DSC) of less than -30°C ; (v) water, (vi) a mono functional polyalkylene ether; (vii) a polyol having a molecular weight of less than $<400\text{ g/mol}$, and (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol, wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%.

[0032] Suitable polyisocyanates (i) include, but are not limited to, aromatic, araliphatic, aliphatic and cycloaliphatic polyisocyanates, such as, for example, 1,4-butylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), pentamethylene diisocyanate (PDI), isophorone diisocyanate (IPDI), 2,2,4- and 2,4,4-trimethyl-hexamethylene diisocyanate, the isomeric bis-(4,4'-isocyanatocyclohexyl)methanes or mixtures thereof of any desired isomer content, 1,4-cyclohexylene diisocyanate, 1,4-phenylene diisocyanate, 2,4- and/or 2,6-toluene diisocyanate or hydrogenated 2,4- and/or 2,6-toluene diisocyanate, 1,5-naphthalene diisocyanate, 2,4'- and 4,4'-diphenylmethane diisocyanate, 1,3- and 1,4-bis-(2-isocyanato-prop-2-yl)-benzene (TMXDI), 1,3-bis(isocyanato-methyl)benzene (XDI), (S)-alkyl 2,6-diisocyanato-hexanoates or (L)-alkyl 2,6-diisocyanatohexanoates.

[0033] Polyisocyanates having a functionality >2 can also be used if desired. Such polyisocyanates include modified diisocyanates having a uretdione, isocyanurate, urethane, allophanate, biuret, iminooxadiazine-dione and/or oxadiazinetriene structure, as well as unmodified polyisocyanates having more than 2 NCO groups per molecule, for example 4-isocyanatomethyl-1,8-octane diisocyanate (nonane triisocyanate) or triphenylmethane-4,4',4''-triisocyanate.

[0034] In some embodiments of the present invention, polyisocyanates or polyisocyanate mixtures containing only aliphatically and/or cycloaliphatically bonded isocyanate groups are used that have a mean functionality of from 2 to 4, such as 2 to 2.6 or 2 to 2.4.

[0035] Polymeric polyols (ii) have a molecular weight M_n of from 400 to 8000 g/mol, such as 400 to 6000 g/mol or, in some cases, 500 to 3000 g/mol, 1000 to 3000 g/mol or 1500 to 3000 g/mol. In certain embodiments, these polymeric polyols have a hydroxyl number of from 20 to 400 mg KOH/g of substance, such as 20 to 300 mg KOH/g of substance, 20 to 200 mg KOH/g of substance or 20 to 100 mg KOH/g of substance. In certain embodiments, these polymeric polyols have a hydroxyl functionality of 1.5 to 6, such as 1.8 to 3 or 1.9 to 2.1. As will be appreciated, the M_n of a polymer containing functional groups, such as a polyol, can, as discussed earlier, be calculated from the functional group number, such as hydroxyl number, which is determined by end-group analysis. "Hydroxyl number", as used herein, is determined according to DIN 53240.

[0036] Exemplary polymeric polyols (ii) include, for example, polyester polyols, polyacrylate polyols, polyurethane polyols, polycarbonate polyols, polyether polyols, polyester polyacrylate polyols, polyurethane polyacrylate polyols, polyurethane polyester polyols, polyurethane polyether polyols, polyurethane polycarbonate polyols, polyester polycarbonate polyols, phenol/formaldehyde resins, on their own or in mixtures.

[0037] Suitable polyether polyols include, for example, the polyaddition products of the styrene oxides, of ethylene oxide, propylene oxide, tetrahydrofuran, butylene oxide, epichlorohydrin, as well as their mixed-addition and graft products, as well as the polyether polyols obtained by condensation of polyhydric alcohols or mixtures thereof and those obtained by alkoxylation of polyhydric alcohols, amines and amino alcohols.

[0038] Suitable polyether polyols often have a hydroxyl functionality of 1.5 to 6.0, such as 1.8 to 3.0, a hydroxyl number of 20 to 700 mg KOH/g solid, such as 20 to 100, 20 to 50 or, in some cases 20 to 40 mg KOH/g solid, and/or a M_n of 400 to 4000 g/mol, such as 100 to 4000 or 1000 to 3000 g/mol.

[0039] Exemplary polyester polyols are the polycondensation products of di- as well as optionally tri- and tetra-ols and di- as well as optionally tri- and tetra-carboxylic acids or hydroxycarboxylic acids or lactones. Instead of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols to prepare the polyesters. Examples of suitable diols are ethylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyalkylene glycols such as polyethylene glycol, further 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and isomers, 1,8-octanediol, neopentyl glycol, 1,4-bis(hydroxymethyl)cyclohexane, 2-methyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, dipropylene glycol, polypropylene glycols, dibutylene glycol, polybutylene glycols, bisphenol A, tetrabromobisphenol A, lactone-modified diols, or hydroxypivalic acid neopentyl glycol ester. In order to achieve a functionality >2 , polyols having a functionality of 3 can optionally be used proportionately, for example trimethylolpropane, glycerol, erythritol, pentaerythritol, trimethylolbenzene or trishydroxyethyl isocyanurate.

[0040] Suitable dicarboxylic acids are, for example, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexane-dicarboxylic acid, adipic acid, azelaic acid, sebacic acid, glutaric acid, tetrachlorophthalic acid, maleic acid, fumaric acid, itaconic acid, malonic acid, suberic acid, 2-methylsuccinic acid, 3,3-diethylglutaric acid, and/or 2,2-dimethylsuccinic acid. Anhydrides of those acids can likewise be used, where they exist. Thus, for the purposes of the present invention, anhydrides are included in the expression "acid". Monocarboxylic acids, such as benzoic acid and hexanecarboxylic acid, can also be used, provided that the mean functionality of the polyol is ≥ 2 . Saturated aliphatic or aromatic acids can be used, such as adipic acid or isophthalic acid. Trimellitic acid is a polycarboxylic acid which can also optionally be used.

[0041] Hydroxycarboxylic acids which can be used as reactants in the preparation of a polyester polyol having terminal hydroxyl groups are, for example, hydroxycaproic acid, hydroxybutyric acid, hydroxydecanoic acid, hydroxystearic acid and the like. Suitable lactones are, for example, ϵ -caprolactone, butyrolactone and their homologues.

[0042] In certain embodiments of the present invention, polymer polyol (ii) comprises or, in some cases, consists essentially of or consists of a polyester diol that is a reaction product of butanediol and one or more of neopentyl glycol, hexanediol, ethylene glycol, and diethylene glycol with adipic acid and one or more of phthalic acid and isophthalic acid, such as polyester polyols that are a reaction product of at least one of butanediol, neopentyl glycol, and hexanediol with at least one of adipic acid and phthalic acid.

[0043] Suitable polyester polyols, such as the foregoing polyester diols, often have a hydroxyl functionality of 1.5 to 6.0, such as 1.8 to 3.0, a hydroxyl number of 20 to 700 mg KOH/gram solid, such as 20 to 100, 20 to 80 or, in some cases 40 to 80 mg KOH/g solid, and/or a M_n of 500 to 3000 g/mol, such as 600 to 2500 g/mol.

[0044] Exemplary polycarbonate polyols are obtainable by reaction of carbonic acid derivatives, for example diphenyl carbonate, dimethyl carbonate or phosgene, with diols. Suitable diols include the diols mentioned earlier with respect to the preparation of polyester polyols. In some cases, the diol component contains from 40 wt.% to 100 wt.% 1,6-hexanediol and/or hexanediol derivatives, often containing ether or ester groups in addition to terminal OH groups, for example products which are obtained by reaction of one mole of hexanediol with at least one mole, preferably from one to two moles, of ϵ -caprolactone or by etherification of hexanediol with itself to form di- or tri-hexylene glycol. Polyether polycarbonate polyols can also be used.

[0045] The third component of the polyurethane dispersion (PUD) is a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group (iii). Exemplary such compounds are those which contain, for example, carboxylate, sulfonate, phosphonate groups or groups which can be converted into the above-mentioned groups by salt formation (potentially anionic groups), and which can be incorporated into the macromolecules by isocyanate-reactive groups, such as hydroxyl or amine groups, that are present.

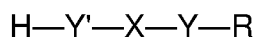
[0046] Suitable anionic or potentially anionic compounds are, for example, mono- and di-hydroxycarboxylic acids, mono- and di-aminocarboxylic acids, mono- and di-hydroxysulfonic acids, mono- and di-aminosulfonic acids as well as mono- and di-hydroxyphosphonic acids or mono- and di-aminophosphonic acids and their salts, such as dimethylolpropionic acid, dimethylolbutyric acid, hydroxypivalic acid, N-(2-aminoethyl)- β -alanine, 2-(2-amino-ethylamino)-ethanesulfonic acid, ethylenediamine-propyl- or -butyl-sulfonic acid, 1,2- or 1,3-propylenediamine-3-ethylsulfonic acid, malic acid, citric acid, glycolic acid, lactic acid. In certain embodiments, the anionic or potentially anionic compounds have at least one of carboxy, carboxylate, and sulfonate groups and have a functionality of from 1.9 to 2.1, such as the salts of 2-(2-aminoethylamino)ethanesulfonic acid.

[0047] In certain embodiments, component (iii) is used in an amount of at least 0.1% by weight, such as at least 1%, or at least 3% by weight and/or no more than 10% by weight, such as no more than 7% by weight, based on the total weight of reactants used to make the polyurethane.

[0048] Amorphous polyesters (iv) are included in the inventive polyurethane dispersion (PUD) which have a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C . In various embodiments, these polyesters have a molecular weight of from 300 to 3000. In certain embodiments, these polyesters have a

molecular weight of approximately 1000. In some embodiments the amorphous polyester (iv) comprises an ortho-phthalic anhydride/1,6-hexane diol.

[0049] Component (vi) is a mono functional polyalkylene ether that contains at least one, in some cases one, hydroxy or amino group. In some embodiments, component (vi) comprises compounds of the formula:



[0050] in which R is a monovalent hydrocarbon radical having 1 to 12 carbon atoms, such as an unsubstituted alkyl radical having 1 to 4 carbon atoms; X is a polyalkylene oxide chain having 5 to 90, such as 20 to 70 chain members, which may comprise at least 40%, such as at least 65%, ethylene oxide units and which in addition to ethylene oxide units may comprise propylene oxide, butylene oxide and/or styrene oxide units; and Y and Y' are each independently oxygen or —NR'— in which R' is H or R, in which R is defined above.

[0051] Mono functional polyalkylene ethers suitable for use in component (vi) may, in some cases, contain 7 to 55 ethylene oxide units per molecule, and can be obtained by alkoxylation of suitable starter molecules, such as, for example, saturated monoalcohols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, the isomeric pentanols, hexanols, octanols and nonanols, n-decanol, n-dodecanol, n-tetradecanol, n-hexadecanol, n-octadecanol, cyclohexanol, the isomeric methyl-cyclohexanols or hydroxymethyl-cyclohexane, 3-ethyl-3-hydroxymethyloxetan or tetrahydrofurfuryl alcohol; diethylene glycol monoalkyl ethers, such as, for example, diethylene glycol monobutyl ether; unsaturated alcohols, such as allyl alcohol, 1,1-dimethyl-allyl alcohol or oleic alcohol; aromatic alcohols, such as phenol, the isomeric cresols or methoxyphenols; araliphatic alcohols, such as benzyl alcohol, anis alcohol or cinnamic alcohol; secondary monoamines, such as dimethylamine, diethylamine, dipropylamine, diisopropylamine, dibutyl-

amine, bis-(2-ethylhexyl)-amine, N-methyl- and N-ethyl-cyclohexylamine or dicyclohexylamine; as well as heterocyclic secondary amines, such as morpholine, pyrrolidine, piperidine or 1H-pyrazole, including mixtures of two or more of any of the foregoing.

[0052] Alkylene oxides suitable for the alkoxylation reaction include, for example, ethylene oxide and propylene oxide, which can be used in the alkoxylation reaction in any desired sequence or alternatively in admixture. In some embodiments, component (vi) comprises a copolymer of ethylene oxide with propylene oxide that contains ethylene oxide in an amount of at least 40% by weight, such as at least 50% by weight, at least 60% by weight or at least 65% by weight and/or up to 90% by weight or up to 80% by weight, based on the total weight of ethylene oxide and propylene oxide. In certain embodiments, the M_n of such a copolymer is 300 g/mol to 6000 g/mol, such as 500 g/mol to 4000 g/mol, such as 1000 g/mol to 3000 g/mol.

[0053] In certain embodiments, component (vi) is used in an amount of at least 1% by weight, such as at least 5%, or at least 10% by weight or no more than 30% by weight, such as no more than 20% by weight, based on the total weight of reactants used to make the polyurethane.

[0054] Component (vii) comprises a polyol having a molecular weight of less than <400 grams/mol. Examples of such polyols include, without limitation, the diols mentioned earlier with respect to the preparation of polyester polyols. In some cases, the polyol having a molecular weight of less than <400 g/mol has up to 20 carbon atoms, such as is the case with, for example, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,3-butylene glycol, cyclohexanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, neopentyl glycol, hydroquinone dihydroxyethyl ether, bisphenol A (2,2-bis(4-hydroxyphenyl)propane), hydrogenated bisphenol A, (2,2-bis(4-hydroxycyclohexyl)propane), trimethylolpropane, glycerol, pentaerythritol and also any

desired mixtures of two or more thereof. Also suitable are ester diols of the specified molecular weight range such as α -hydroxybutyl- ϵ -hydroxycaproic acid ester, ω -hydroxyhexyl- γ -hydroxybutyric acid ester, β -hydroxyethyl adipate or bis(β -hydroxyethyl) terephthalate.

[0055] In certain embodiments, component (vii) is used in an amount of at least 1% by weight, such as at least 2%, or at least 3% by weight and/or no more than 20% by weight, such as no more than 10% or no more than 5% by weight, based on the total weight of reactants used to make the polyurethane.

[0056] Component (viii) is used for chain extension and includes di- or poly-amines as well as hydrazides, for example ethylenediamine, 1,2- and 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, isophoronediamine, isomer mixture of 2,2,4- and 2,4,4-trimethyl-hexamethylenediamine, 2-methylpentamethylenediamine, diethylenetriamine, 1,3- and 1,4-xylylenediamine, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and -1,4-xylylenediamine and 4,4-diaminodicyclohexylmethane, dimethylethylenediamine, hydrazine or adipic acid dihydrazide. Also suitable for use are compounds which contain active hydrogen of different reactivity towards NCO groups, such as compounds which contain, in addition to a primary amino group, also secondary amino groups or, in addition to an amino group (primary or secondary), also OH groups. Examples thereof are primary/secondary amines, such as 3-amino-1-methyl-aminopropane, 3-amino-1-ethylaminopropane, 3-amino-1-cyclohexylaminopropane, 3-amino-1-methylaminobutane, also alkanolamines such as N-aminoethylethanolamine, ethanolamine, 3-aminopropanol or neopentanolamine.

[0057] In certain embodiments, component (viii) is used in an amount of at least 1% by weight, such as at least 3% or at least 5% by weight and no more than 10% by weight, such as no more than 8% or, in some cases, no more than 7% by weight, based on the total weight of reactants used to make the polyurethane.

[0058] In various non-limiting embodiments of the present invention, the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%. In certain embodiments, the hard block content is from 50% to 60% and in a preferred embodiment, the hard block content is from greater than 55% to 60%.

[0059] Any of a variety of processes can be used to prepare the aqueous polyurethane dispersion (PUD) of the present invention, such as the prepolymer mixing method, acetone method or melt dispersing method, each of which will be understood by a person skilled in the art of making aqueous polyurethane dispersions. For example, in some embodiments, the aqueous polyurethane dispersions of the present invention may be produced by the acetone method, such as is described, for example, in U.S. Patent Application Publication No. 2007/0167565 A1 at [0057]-[0073], the cited portion of which being incorporated herein by reference.

[0060] In certain embodiments, the resin solids content of the aqueous polyurethane dispersion (PUD) prepared by any of these methods is at least 20% by weight, such as at least 25% or at least 30% by weight or no more than 65% by weight, such as no more than 50% or no more than 45% by weight, based on the total weight of the dispersion.

[0061] Among the possible applications for the inventive aqueous polyurethane dispersion (PUD) is in or as a coating or paint for application on a frame of an architectural article, such as a vinyl door, door frame, window, window frame, window surrounds, window shutters, railing, gates, pillars, arbors, pergolas, trellises, gazebos, posts, fencing, cladding and siding, particularly those that are constructed of a material such as polyvinylchloride (PVC). In certain embodiments, the aqueous polyurethane dispersion (PUD) of the present invention may produce a

cured coating that, when used on a frame of an architectural article, such as a door or window, meets or exceeds many if not all of the requirements of AAMA specification 615-13, "Voluntary Specification, Performance Requirements and Test Procedures for Superior Performing Organic Coatings on Plastic Profiles", (referred to herein as "AAMA 615-13"). For example, cured coatings made from the aqueous polyurethane dispersion (PUD) of the present invention, when deposited over a low surface energy synthetic substrate, such as polyvinylchloride (PVC), may pass the detergent resistance test described in AAMA 615-13.

[0062] As used herein, "vinyl" means materials made by polymerizing an alkene group into a chain. Examples of vinyl compounds include, but are not limited to, polyvinylchloride, polystyrene, polyvinyl acetate, polyvinyl alcohol, and polyacrylonitrile.

[0063] As used herein, "low surface energy", when used to describe a substrate, in certain embodiments means a material having a surface energy of from 12 mJ/m² to 60 mJ/m²; in other embodiments, the material has a surface energy of from 25 mJ/m² to 45 mJ/m²; and in yet other embodiments, the material has a surface energy of 30 mJ/m² to 40 mJ/m². Representative low surface energy materials include the vinyl materials listed above and polyhexafluoropropylene, polytetrafluoroethylene, poly(vinylidene fluoride), poly(chlorotrifluoroethylene), polyethylene, polypropylene, poly(methylmethacrylate), polyamide, poly(vinylidene chloride), poly(ethylene terephthalate), epoxy, phenol-resorcinol resin, styrene-butadiene rubber, and acrylonitrile-butadiene rubber.

[0064] The aqueous polyurethane dispersions (PUDs), coatings, adhesives, and sealants of the present invention may further include any of a variety of additives such as defoamers, devolatilizers, thickeners, flow control additives, colorants (including pigments and dyes), surfactants, dispersants, and neutralizers as is known to those skilled in the art.

[0065] The aqueous polyurethane dispersions (PUDs) and coatings of the present invention may be admixed and combined with the conventional paint-technology binders, auxiliaries and additives, selected from the group of pigments, dyes, matting agents, flow control additives, wetting additives, slip additives, pigments, including metallic effect pigments, fillers, nanoparticles, light stabilizing particles, anti-yellowing additives, thickeners, and additives for reducing the surface tension.

[0066] The aqueous polyurethane dispersions (PUDs), coatings, adhesives, and sealants according to the invention can be applied to the substrate by the conventional techniques, such as, spraying, rolling, flooding, printing, knife-coating, pouring, brushing and dipping.

EXAMPLES

[0067] The non-limiting and non-exhaustive examples that follow are intended to further describe various non-limiting and non-exhaustive embodiments without restricting the scope of the embodiments described in this specification. All quantities given in “parts” and “percents” are understood to be by weight, unless otherwise indicated.

POLYOL A	ortho-phthalic anhydride/1,6-hexane diol, having a molecular weight of 1000, commercially available from Stepan Co. as STEPANPOL PC-1028-115;
POLYOL B	adipic acid/1,6-hexane diol, having a molecular weight of 840, commercially available from Covestro as DESMOPHEN 84H;
POLYOL C	polytetramethylene ether glycol (PTMEG), having a molecular weight of 1000, commercially available from INVISTA as TERATHANE 1000;
POLYOL D	a polycarbonate diol/1,6-hexanediol, having a molecular weight of 1000, commercially available from Covestro as DESMOPHEN C2100;

POLYOL E	a DMC-catalyzed, polyether polyol based on propylene glycol and propylene oxide having a hydroxyl number of about 111 mg KOH/g and a functionality of about 2, commercially available from Covestro as ARCOL PPG 1000;
POLYOL F	a butyl-diglycol based PO/EO (15.6%/63.5%) monol capped with EO (20.9%) having a hydroxyl number of about 25 mg KOH/g, commercially available from Covestro as POLYETHER LB-25;
ISOCYANATE A	4,4'-dicyclohexylmethane diisocyanate having an NCO group content of about 31.8% and a functionality of about 2, commercially available from Covestro as DESMODUR W;
SURFACTANT A	a nonionic wetting agent and molecular defoamer (75% active liquid in ethylene glycol) commercially available from Air Products as SURFYNOL 104H;
ADDITIVE A	dimethylolpropionic acid (DMPA);
ADDITIVE B	neopentylglycol (NPG);
SOLVENT A	n-methyl-2-pyrrolidone (NMP);
ADDITIVE C	triethylamine (TEA);
EXTENDER A	diethylenetriamine (DETA);
EXTENDER B	hydrazine hydrate, 64% (HyHy); and
EXTENDER C	ethylenediamine (EDA).

Example 1

[0068] Table I provides the formulations used in the examples along with their properties. Each polyurethane dispersion was made by charging the specified amounts of the relevant POLYOL A-E, POLYOL F and

ADDITIVE A and ADDITIVE B to a reaction vessel and heating the vessel to 70°C. The specified amount of ISOCYANTE A was added to the vessel and the vessel observed for an exothermic reaction. When the exothermic reaction was observed, the vessel was maintained at 95°C. The mixture was sampled and assessed for percent NCO. The mixture was cooled to 80°C and another sample removed and assessed for percent NCO. The specified amounts of SOLVENT A and ADDITIVE C were added to the mixture and mixed for 20 minutes. The resultant prepolymer was dispersed in the specified amount of water along with the specified amount of SURFACTANT A. EXTENDERS A, B and C were added dropwise and the mixture mixed for one hour while cooling to room temperature. The polyurethane dispersion was filtered through a 50 µm filter before use.

Table I

	Ex. A	Ex. B	Ex. C	Ex. D	Ex. E
POLYOL A	664.7				
POLYOL B		259.2			
POLYOL C			264.3		
POLYOL D				264.3	
POLYOL E					264.1
POLYOL F	57.7	22.5	22.9	22.9	22.9
ADDITIVE A	63.3	25.3	25.3	25.3	25.3
ADDITIVE B	68.9	26.9	27.4	27.4	27.4
SOLVENT A	350	139.90	140	140	139.93
ADDITIVE C	47.8	19.1	19.1	19.1	19.16
EXTENDER A	21.5	8.4	8.6	8.6	8.55
EXTENDER B	21.5	8.4	8.6	8.6	8.55
EXTENDER C	19.4	7.6	7.7	7.7	8.55
WATER, DI	2885.9	1157.90	1157.80	1157.80	1157.30
SURFACTANT A	8.6	3.4	3.4	3.4	3.42
ISOCYANATE A	790.8	321.5	314.9	314.9	314.77
Properties					
% NCO	5.04	4.88	5.04	5.04	5.04
NCO/OH+NH	1.04	1.03	1.04	1.04	1.03
NCO:OH	1.65	1.6	1.65	1.65	1.65
%NMP	7.0	7.0	7.0	7.0	7.00
%COOH	1.25	1.25	1.25	1.25	1.26
% Solids	34.00	33.84	34.4	34.42	33.86
Chain ext. %	90.19	91.09	90.02	90.02	93.08
% neutralization	100	100	100	100	100.21

[0069] Films were made from the formulations for testing. The film thickness was 6 mils (wet) and the films were dried at 50°C for 10 minutes (except for drying time at room temperature). All testing followed after an additional seven day rest at ambient temperature. When films were made on vinyl substrate for AAMA 615-13 test (Table IV), the following surface preparation method was conducted: the vinyl substrate was wiped with lacquer thinner, IPA and acetone.

[0070] Dry times were measured by a dry time recorder (DT-5040) manufactured by the Paul N. Gardner Co., Inc. For assessing film hardness, pendulum hardness was measured by a pendulum damping tester (Model 299/300) manufactured by Erichsen GmbH & Co. KG and microhardness was measured by a microhardness instrument (Fisherscope HM 2000) manufactured by Fischer Technology Inc.

[0071] For determining flexibility, mandrel bending was measured by conical mandrel bend test and by BYK impact test.

[0072] As can be appreciated by reference to Table II, there appeared to be no significant difference with dry time, film hardness (on glass) or flexibility possibly due to higher hard block content with all aqueous polyurethane dispersions (PUDs).

[0073] Chemical resistance was measured by a 24-hour spot test of the indicated chemical on glass.

[0074] Humidity resistance was measured by exposing the film to 38°C at 100% Relative Humidity for 168 hours and assessing for blisters according to ASTM D714.

[0075] As can be appreciated by reference to Table III, the POLYOL A-based aqueous polyurethane dispersion (PUD) had comparable chemical resistance to that of the POLYOL D-based aqueous polyurethane dispersion (PUD), but the POLYOL A-based aqueous polyurethane dispersion (PUD) showed better humidity resistance.

[0076] Pencil hardness on vinyl was determined according to ASTM D3363.

[0077] Adhesion on vinyl was determined by the crosshatch adhesion test as described in ASTM D 3359.

[0078] Detergent resistance was measured as described in AAMA 615-13 after 72 hours immersion at 38°C for its effect on gloss retention as determined by a gloss meter (Micro-TRI-gloss) manufactured by BYK

Gardner GmbH; Delta E as determined by a spectrophotometer (Color i7 manufactured by X-rite, Inc. as described in ASTM D 2244; Appearance after test as determined by visual examination; and Adhesion after test as determined by crosshatch adhesion test as described in ASTM D 3359.

[0079] Gloss retention was determined by a gloss meter (Micro-TRI-gloss) manufactured by BYK Gardner Corp. and Delta E as determined by a spectrophotometer (Color i7) manufactured by X-rite, Inc. as described in ASTM D 2244 were also conducted to measure each of nitric acid and muriatic acid resistances.

[0080] As can be appreciated by reference to Table IV, the POLYOL A-based aqueous polyurethane dispersion (PUD) has superior detergent resistance and higher film hardness on vinyl substrate in AAMA 615-13.

Table II

PUD based on POLYOL	A	B	C	D	E
Dry time					
Set-to-touch (minutes)	30	20	15	15	15
Dry-hard (minutes)	155	120	180	135	90
Film hardness					
Pendulum hardness (sec)	87	120	90	137	76
Micro hardness (N/mm²)	38.3	49.8	37.3	57.0	30.3
Flexibility					
Mandrel bend test @ 1/8 inch	Pass	Pass	Pass	Pass	Pass
BYK impact test (Direct) (in lbs.	90	100	90	90	90

Table III

PUD based on POLYOL	A	B	C	D	E
Chemical resistance					
Muriatic acid (10%)	No effect	No effect	No effect	No effect	Soften/recover within 1 hour
Nitric acid (10%)	No effect	Soften	Soften/recover within 1 hour	No effect	Soften/recover within 1 hour
Sodium hydroxide (10%)	No effect	Slightly soften/recover within 1 hour	No effect	No effect	Slightly soften/recover within 1 hour
IPA	Soften/recover within 1 hour	Complete removal	Soften/recover within 1 hour	Soften/recover within 1 hour	Complete removal
Detergent	No effect	No effect	Soften/recover within 1 hour	No effect	Soften/recover within 1 hour
Humidity resistance					
Blister	None	Few	Medium	Medium	Medium

Table IV

PUD based on POLYOL	A	B	C	D	E
Pencil hardness on vinyl	3H	F	H	F	F
Adhesion on vinyl	5B	5B	5B	5B	5B
Detergent resistance					
Gloss retention (%)	114	NT	NT	79	NT
Delta E	0.2	NT	NT	0.2	NT
Appearance after test	No blister	Severe blister	Deteriorated	Blister	Deteriorated
Adhesion after test	No loss of adhesion	Loss of adhesion	Loss of adhesion	Loss of adhesion	Loss of adhesion
Nitric acid resistance					
Gloss retention (%)	126	141	127	134	137
Delta E	0.2	0.1	0.1	0.2	0.1
Muriatic acid resistance					
Gloss retention (%)	105	102	106	107	104
Delta E	0.2	0.4	0.2	0.3	0.2

[0081] “Glass transition temperature” (T_g) is given in °C and was determined by differential scanning calorimetry. Differential scanning calorimetry (DSC) was conducted on each of the polyols (Table V) and each of the aqueous polyurethane dispersions (PUDs) made with the respective polyols (Table VI) to determine the glass transition temperature of each material. The heating rate was 20°C/min.

[0082] FIG. 1 is a differential scanning calorimetry (DSC) thermogram of POLYOL A. FIG. 2 is a DSC thermogram of POLYOL B. FIG. 3 is a DSC thermogram of POLYOL C. FIG. 4 is a DSC thermogram of POLYOL E. FIG. 5 is a DSC thermogram of POLYOL D.

[0083] As can be appreciated by reference to Table V and FIGS. 1, 2, 3, 4 and 5, POLYOL A (ortho-phthalic based) and POLYOL E (polypropylene glycol based) are amorphous. Others such as POLYOL B (adipate based), POLYOL C (PTMEG based) and POLYOL D (polycarbonate based) are crystalline.

Table V

Sub-DSC -120 to 100°C						
Sample	First Heat		Cooling	Reheat		Morphology
	T _g (ΔC _p) °C (J/g°C)	T _m (ΔH _m) °C (J/g)	T _c (ΔH _c) °C (J/g)	T _g (ΔC _p) °C (J/g°C)	T _m (ΔH _m) °C (J/g)	
POLYOL A	-34 (0.43)			-36 (0.41)		Amorphous
POLYOL B		7, 27, 42, 48* (105.24)	4, 21, 27, 30* (94.15)		7, 25, 45* (95.47)	Crystalline
POLYOL C		14, 22* (93.79)	-1 (87.93)		17, 22* (101.85)	Crystalline
POLYOL D		16, 35, 42, 45* (76.78)	16 (64.24)		4, 20, 40, 44* (65.98)	Crystalline
POLYOL E	-70 (0.63)			-70 (0.62)		Amorphous

*main peak in a multiple peak event

[0084] FIGS. 6 and 7 are DSC thermograms of films, each made from an identical polyurethane dispersion formulation containing a different one of POLYOLS A, B, C, D, and E.

Table VI

	As-received samples 25 to 150°C	Sub-DSC -65 to 100°C
Sample PUD Films	First Heat	Reheat
	T _m (ΔH_m) °C (J/g)	T _g (ΔC_p) °C (J/g°C)
PUD based on POLYOL A	59 (2.82)	9 (0.07)
PUD based on POLYOL B	63 (2.71)	-34 (0.06)
PUD based on POLYOL C	65 (2.67)	-29 (0.04)
PUD based on POLYOL D	65 (1.68)	-21 (0.06)
PUD based on POLYOL E	67 (2.20)	-25 (0.07)

[0085] As can be appreciated by reference to Table VI and FIGS. 6 and 7, the polyurethane dispersion based on POLYOL A (ortho-phthalic base) exhibited the highest glass transition temperature (T_g) at 9°C among the five films tested. The others were below - 20°C.

[0086] Betadine stain resistance for aqueous polyurethane dispersions (PUDs) which were made with the polyols listed in Table VII was assessed by a chemical spot test. As can be appreciated by reference to Table VII, the POLYOL A-based aqueous polyurethane dispersion (PUD) had better betadine stain resistance than any other aqueous polyurethane dispersions (PUDs).

Table VII

	POLYOL A	POLYOL B	POLYOL C	POLYOL D	POLYOL E
1 hour	No effect	Slightly stained	Stain	Slightly stained	Stain
4 hours	No effect	Stain	Stain	Slightly stained	Stain

Table VIII

Hard Block on TRS (%)	60			55			51		
Chain Ext %	80	88	95	80	88	95	80	88	95.0
Pencil hardness									
+ 10 days	3H	6H	3H	4H	3H	2H	NT	H	H
Detergent resistance									
Gloss retention (%)	143.5	172.6	189.0	205.6	173.6	Failed	NT	Failed	Failed
Delta E	0.5	0.6	0.8	0.6	0.6	Failed	NT	Failed	Failed

[0087] This specification has been written with reference to various non-limiting and non-exhaustive embodiments. However, it will be recognized by persons having ordinary skill in the art that various substitutions, modifications, or combinations of any of the disclosed embodiments (or portions thereof) may be made within the scope of this specification. Thus, it is contemplated and understood that this specification supports additional embodiments not expressly set forth herein. Such embodiments may be obtained, for example, by combining, modifying, or reorganizing any of the disclosed steps, components, elements, features, aspects, characteristics, limitations, and the like, of the various non-limiting embodiments described in this specification. In this manner, Applicants reserve the right to amend the claims during prosecution to add features as variously described in this specification, and such amendments comply with the requirements of 35 U.S.C. §112(a), and 35 U.S.C. §132(a).

[0088] Various aspects of the subject matter described herein are set out in the following numbered clauses:

[0089] Clause 1. An aqueous polyurethane dispersion (PUD) comprising the reaction product of: (i) a polyisocyanate; (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol; (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group; (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C; (v) water; (vi) a mono functional polyalkylene ether; (vii) a polyol having a molecular weight of less than <400 g/mol, and (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol, wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%.

[0090] Clause 2. The aqueous polyurethane dispersion (PUD) according to Clause 1, wherein the amorphous polyester (iv) comprises ortho-phthalic anhydride.

[0091] Clause 3. The aqueous polyurethane dispersion (PUD) according to one of Clauses 1 and 2, wherein the dispersion has a hard block content of 50% to 60%.

[0092] Clause 4. The aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 3, wherein the dispersion has a hard block content of greater than 55% to 60%.

[0093] Clause 5. The aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 4, wherein the amorphous polyester (iv) has a molecular weight of 300 to 3000.

[0094] Clause 6. The aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 5, wherein the amorphous polyester (iv) has a molecular weight of 1000.

[0095] Clause 7. The aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 6, wherein the polyisocyanate (i) is selected from the group consisting of 1,6-hexamethylene diisocyanate (HDI), pentamethylene diisocyanate (PDI), isophorone diisocyanate (IPDI), 2,2,4- and 2,4,4-trimethyl-hexamethylene diisocyanate, isomeric bis-(4,4'-isocyanatocyclohexyl)methanes or mixtures thereof of any desired isomer content, 1,4-cyclohexylene diisocyanate, 1,4-phenylene diisocyanate, 2,4- and 2,6-toluene diisocyanate or hydrogenated 2,4- and 2,6-toluene diisocyanate, 1,5-naphthalene diisocyanate, 2,4'- and 4,4'-diphenylmethane diisocyanate, 1,3- and 1,4-bis-(2-isocyanato-prop-2-yl)-benzene (TMXDI), 1,3-bis(isocyanato-methyl)benzene (XDI), and (S)-alkyl 2,6-diisocyanato-hexanoates or (L)-alkyl 2,6-diisocyanatohexanoates.

[0096] Clause 8. One of a coating, an adhesive, and a sealant comprising the aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 7.

[0097] Clause 9. A coating containing the aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 7, wherein the coating passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color change of 5 delta E, with no blistering, with no loss of adhesion after testing and has a pencil hardness according to ASTM D3363 of at least 3H.

[0098] Clause 10. A coating containing the aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 7, wherein the coating exhibits no staining by betadine after four hours.

[0099] Clause 11. A coating containing the aqueous polyurethane dispersion (PUD) according to one of Clauses 1 to 7, wherein the coating passes humidity resistance testing according to ASTM D714 with no blistering.

[0100] Clause 12. The coating according to one of Clauses 9 to 11 having a pencil hardness according to ASTM D3363 of from 3H to 6H.

[0101] Clause 13. A substrate having applied thereto the coating according to one of Clauses 9 to 12.

[0102] Clause 14. The substrate according to Clause 13, wherein the substrate is polyvinylchloride.

[0103] Clause 15. The substrate according to Clause 14, wherein the substrate is selected from the group consisting of floors, windows, doors, window frames, door frames, window shutters, window surrounds railing, gates, pillars, arbors, pergolas, trellises, gazebos, posts, fencing, pipes and fittings, wire and cable insulation, automobile components, credit cards, cladding and siding.

[0104] Clause 16. A coating containing an aqueous polyurethane dispersion (PUD), wherein the coating passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color change of 5 delta E, with no blistering and no loss of adhesion after testing, wherein the coating exhibits no staining by betadine

after four hours, wherein the coating passes humidity resistance testing according to ASTM D714 with no blistering and wherein the coating has a pencil hardness according to ASTM D3363 of at least 3H.

[0105] Clause 17. The coating according to Clause 16, wherein the aqueous polyurethane dispersion (PUD) comprises the reaction product of: (i) a polyisocyanate; (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol; (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group; (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C; (v) water; (vi) a mono function al polyalkylene ether; (vii) a polyol having a molecular weight of less than <400 g/mol, and (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol, wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%.

[0106] Clause 18. The coating according to Clause 17, wherein the amorphous polyester (iv) comprises ortho-phthalic anhydride.

[0107] Clause 19. A paint comprising an aqueous polyurethane dispersion (PUD), wherein the paint passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color change of 5 delta E, no blistering and no loss of adhesion after testing, wherein the paint exhibits no staining by betadine after four hours, wherein the paint passes humidity resistance testing according to ASTM D714 with no blistering and wherein the coating has a pencil hardness according to ASTM D3363 of at least 3H.

[0108] Clause 20. The paint according to Clause 19, wherein the aqueous polyurethane dispersion (PUD) comprises the reaction product of: (i) a polyisocyanate; (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol; (iii) a compound comprising at

least one isocyanate-reactive group and an anionic group or potentially anionic group; (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C; (v) water; (vi) a mono function al polyalkylene ether; (vii) a polyol having a molecular weight of less than <400 g/mol, and (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol, wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%.

[0109] Clause 21. The paint according to Clause 20, wherein the amorphous polyester (iv) comprises ortho-phthalic anhydride.

[0110] Clause 22. A substrate having applied thereto the paint according to one of Clauses 19 to 21.

[0111] Clause 23. The substrate according to Clause 22, wherein the substrate comprises polyvinylchloride.

[0112] Clause 24. The substrate according to Clause 23, wherein the substrate is selected from the group consisting of floors, windows, doors, window frames, window surrounds, door frames, window shutters, railing, gates, pillars, arbors, pergolas, trellises, gazebos, posts, fencing, pipes and fittings, wire and cable insulation, automobile components, cladding and siding.

[0113] Clause 25. The paint according to Clause 19, further including at least one of binders, auxiliaries, pigments, dyes, matting agents, flow control additives, wetting additives, slip additives, metallic effect pigments, fillers, nanoparticles, light stabilizing particles, anti-yellowing additives, thickeners, and additives for reducing surface tension.

[0114] Clause 26. A low surface energy substrate having applied thereto a coating containing an aqueous polyurethane dispersion (PUD), wherein the coating passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color

change of 5 delta E, no blistering and no loss of adhesion after testing, wherein the coating exhibits no staining by betadine after four hours, wherein the coating passes humidity resistance testing according to ASTM D714 with no blistering and wherein the coating has a pencil hardness according to ASTM D3363 of at least 3H.

[0115] Clause 27. The low surface energy substrate according to Clause 26, wherein the substrate is selected from the group consisting of polyvinylchloride, polystyrene, polyvinyl acetate, polyvinyl alcohol, and polyacrylonitrile.

[0116] Clause 28. The low surface energy substrate according to one of Clauses 26 and 27, wherein the wherein the aqueous polyurethane dispersion (PUD) comprises the reaction product of: (i) a polyisocyanate; (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol; (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group; (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry of less than -30°C ; (v) water, (vi) a mono functional polyalkylene ether; (vii) a polyol having a molecular weight of less than <400 g/mol, and (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol, wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry of 0°C to 20°C and a hard block content of greater than 50%.

[0117] Clause 29. The low surface energy substrate according to one of Clauses 26 to 28, wherein the substrate has a surface energy of from 12 mJ/m^2 to 60 mJ/m^2 .

[0118] Clause 30. The low surface energy substrate according to one of Clauses 26 to 29, wherein the substrate has a surface energy of from 25 mJ/m^2 to 45 mJ/m^2 .

[0119] Clause 31. The low surface energy substrate according to one of Clauses 26 to 30, wherein the substrate has a surface energy of 30 mJ/m² to 40 mJ/m².

WHAT IS CLAIMED IS:

1. An aqueous polyurethane dispersion (PUD) comprising the reaction product of:

- (i) a polyisocyanate;
- (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol;
- (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group;
- (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C ;
- (v) water;
- (vi) a mono functional polyalkylene ether;
- (vii) a polyol having a molecular weight of less than <400 g/mol, and
- (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol,

wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%.

2. The aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the amorphous polyester (iv) comprises ortho-phthalic anhydride.

3. The aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the dispersion has a hard block content of 50% to 60%.

4. The aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the dispersion has a hard block content of greater than 55% to 60%.

5. The aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the amorphous polyester (iv) has a molecular weight of 300 to 3000.
6. The aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the amorphous polyester (iv) has a molecular weight of 1000.
7. The aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the polyisocyanate (i) is selected from the group consisting of 1,6-hexamethylene diisocyanate (HDI), pentamethylene diisocyanate (PDI), isophorone diisocyanate (IPDI), 2,2,4- and 2,4,4-trimethyl-hexamethylene diisocyanate, isomeric bis-(4,4'-isocyanatocyclohexyl)methanes or mixtures thereof of any desired isomer content, 1,4-cyclohexylene diisocyanate, 1,4-phenylene diisocyanate, 2,4- and 2,6-toluene diisocyanate or hydrogenated 2,4- and 2,6-toluene diisocyanate, 1,5-naphthalene diisocyanate, 2,4'- and 4,4'-diphenylmethane diisocyanate, 1,3- and 1,4-bis-(2-isocyanato-prop-2-yl)-benzene (TMXDI), 1,3-bis(isocyanato-methyl)benzene (XDI), and (S)-alkyl 2,6-diisocyanato-hexanoates or (L)-alkyl 2,6-diisocyanatohexanoates.
8. One of a coating, an adhesive, and a sealant comprising the aqueous polyurethane dispersion (PUD) according to Claim 1.
9. A coating containing the aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the coating passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color change of 5 delta E, with no blistering, with no loss of adhesion after testing and has a pencil hardness according to ASTM D3363 of at least 3H.
10. A coating containing the aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the coating exhibits no staining by betadine after four hours.

11. A coating containing the aqueous polyurethane dispersion (PUD) according to Claim 1, wherein the coating passes humidity resistance testing according to ASTM D714 with no blistering.
12. The coating according to Claim 9 having a pencil hardness according to ASTM D3363 of from 3H to 6H.
13. A substrate having applied thereto the coating according to Claim 9.
14. The substrate according to Claim 13, wherein the substrate is polyvinylchloride.
15. The substrate according to Claim 14, wherein the substrate is selected from the group consisting of floors, windows, doors, window frames, door frames, window shutters, window surrounds railing, gates, pillars, arbors, pergolas, trellises, gazebos, posts, fencing, pipes and fittings, wire and cable insulation, automobile components, credit cards, cladding and siding.
16. A coating containing an aqueous polyurethane dispersion (PUD), wherein the coating passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color change of 5 delta E, with no blistering and no loss of adhesion after testing,
wherein the coating exhibits no staining by betadine after four hours,
wherein the coating passes humidity resistance testing according to ASTM D714 with no blistering and
wherein the coating has a pencil hardness according to ASTM D3363 of at least 3H.

17. The coating according to Claim 16, wherein the aqueous polyurethane dispersion (PUD) comprises the reaction product of:
- (i) a polyisocyanate;
 - (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol;
 - (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group;
 - (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C ;
 - (v) water;
 - (vi) a mono functional polyalkylene ether;
 - (vii) a polyol having a molecular weight of less than <400 g/mol, and
 - (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol,

wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%.

18. The coating according to Claim 17, wherein the amorphous polyester (iv) comprises ortho-phthalic anhydride.

19. A paint comprising an aqueous polyurethane dispersion (PUD), wherein the paint passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color change of 5 delta E, no blistering and no loss of adhesion after testing,

wherein the paint exhibits no staining by betadine after four hours,

wherein the paint passes humidity resistance testing according to ASTM D714 with no blistering and

wherein the coating has a pencil hardness according to ASTM D3363 of at least 3H.

20. The paint according to Claim 19, wherein the aqueous polyurethane dispersion (PUD) comprises the reaction product of:

- (i) a polyisocyanate;
- (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol;
- (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group;
- (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of less than -30°C ;
- (v) water;
- (vi) a mono functional polyalkylene ether;
- (vii) a polyol having a molecular weight of less than <400 g/mol, and
- (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol,

wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC) of 0°C to 20°C and a hard block content of greater than 50%.

21. The paint according to Claim 20, wherein the amorphous polyester (iv) comprises ortho-phthalic anhydride.

22. A substrate having applied thereto the paint according to Claim 19.

23. The substrate according to Claim 22, wherein the substrate comprises polyvinylchloride.

24. The substrate according to Claim 23, wherein the substrate is selected from the group consisting of floors, windows, doors, window frames, window surrounds, door frames, window shutters, railing, gates, pillars, arbors, pergolas, trellises, gazebos, posts, fencing, pipes and

fittings, wire and cable insulation, automobile components, cladding and siding.

25. The paint according to Claim 19, further including at least one of binders, auxiliaries, pigments, dyes, matting agents, flow control additives, wetting additives, slip additives, metallic effect pigments, fillers, nanoparticles, light stabilizing particles, anti-yellowing additives, thickeners, and additives for reducing surface tension.

26. A low surface energy substrate having applied thereto a coating containing an aqueous polyurethane dispersion (PUD), wherein the coating passes detergent resistance testing according to AAMA 615-13 with a minimum 90% gloss retention, a maximum color change of 5 delta E, no blistering and no loss of adhesion after testing, wherein the coating exhibits no staining by betadine after four hours, wherein the coating passes humidity resistance testing according to ASTM D714 with no blistering and wherein the coating has a pencil hardness according to ASTM D3363 of at least 3H.

27. The low surface energy substrate according to Claim 26, wherein the substrate is selected from the group consisting of polyvinylchloride, polystyrene, polyvinyl acetate, polyvinyl alcohol, and polyacrylonitrile.

28. The low surface energy substrate according to Claim 26, wherein the wherein the aqueous polyurethane dispersion (PUD) comprises the reaction product of:

- (i) a polyisocyanate;
- (ii) a polymeric polyol having a number average molecular weight of 400 to 8,000 g/mol;

- (iii) a compound comprising at least one isocyanate-reactive group and an anionic group or potentially anionic group;
- (iv) an amorphous polyester having a glass transition temperature (T_g) as determined by differential scanning calorimetry of less than -30°C ;
- (v) water,
- (vi) a mono functional polyalkylene ether;
- (vii) a polyol having a molecular weight of less than $<400\text{ g/mol}$, and
- (viii) a polyamine or amino alcohol having a molecular weight of 32 to 400 g/mol,

wherein the aqueous polyurethane dispersion (PUD) has a glass transition temperature (T_g) as determined by differential scanning calorimetry of 0°C to 20°C and a hard block content of greater than 50 %.

29. The low surface energy substrate according to Claim 26, wherein the substrate has a surface energy of from 12 mJ/m^2 to 60 mJ/m^2 .

30. The low surface energy substrate according to Claim 26, wherein the substrate has a surface energy of from 25 mJ/m^2 to 45 mJ/m^2 .

31. The low surface energy substrate according to Claim 26, wherein the substrate has a surface energy of 30 mJ/m^2 to 40 mJ/m^2 .

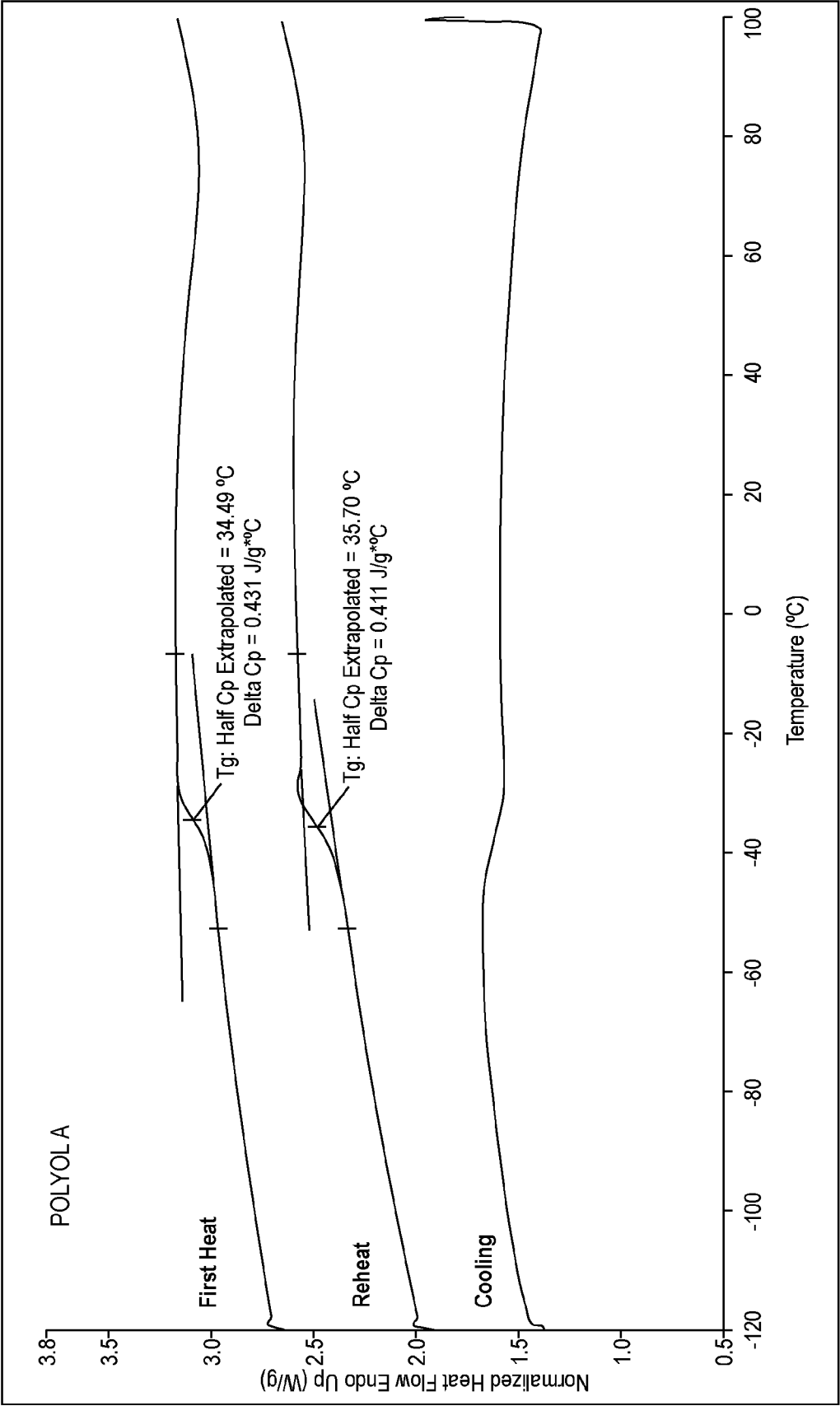


FIG. 1

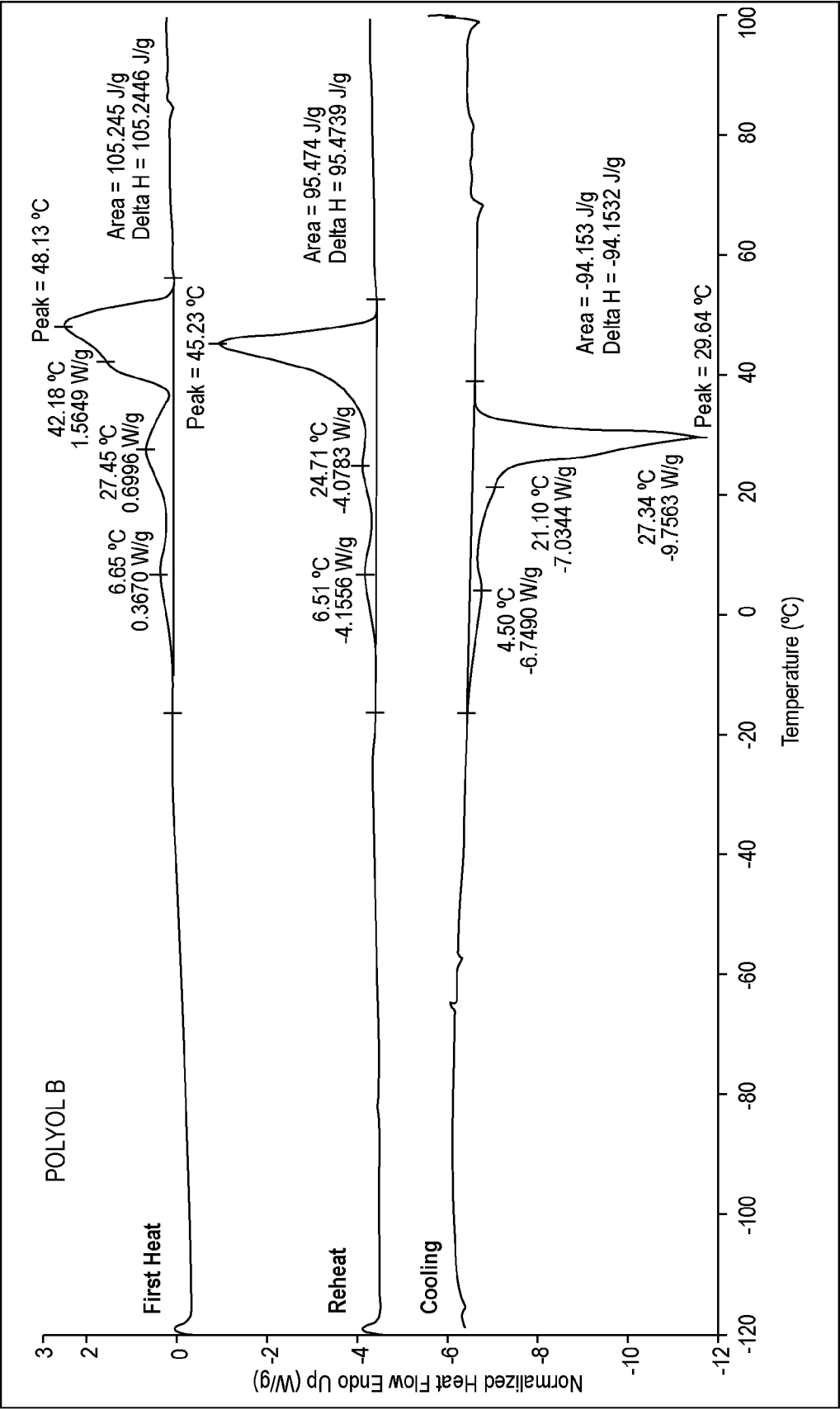


FIG. 2

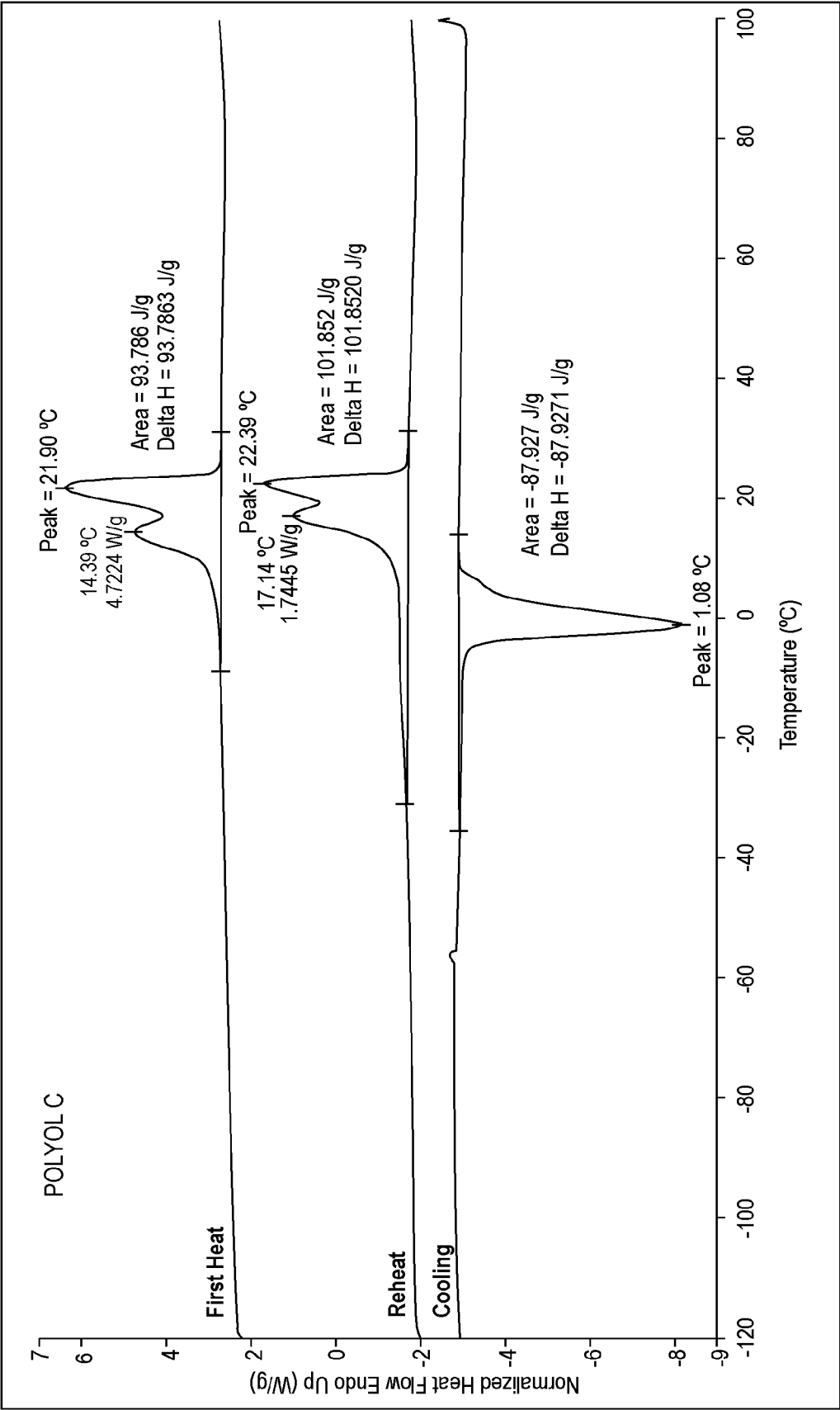


FIG. 3

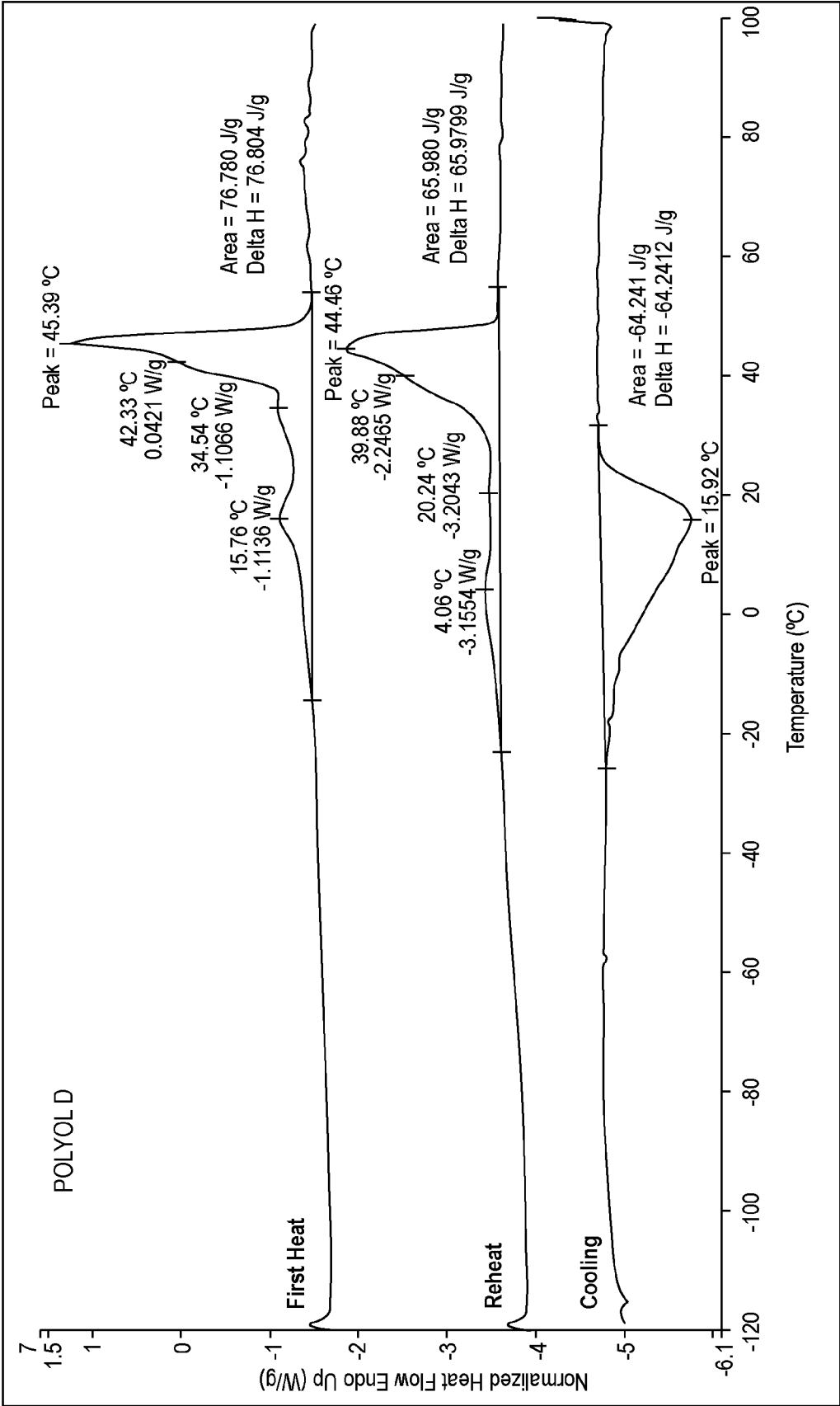


FIG. 4

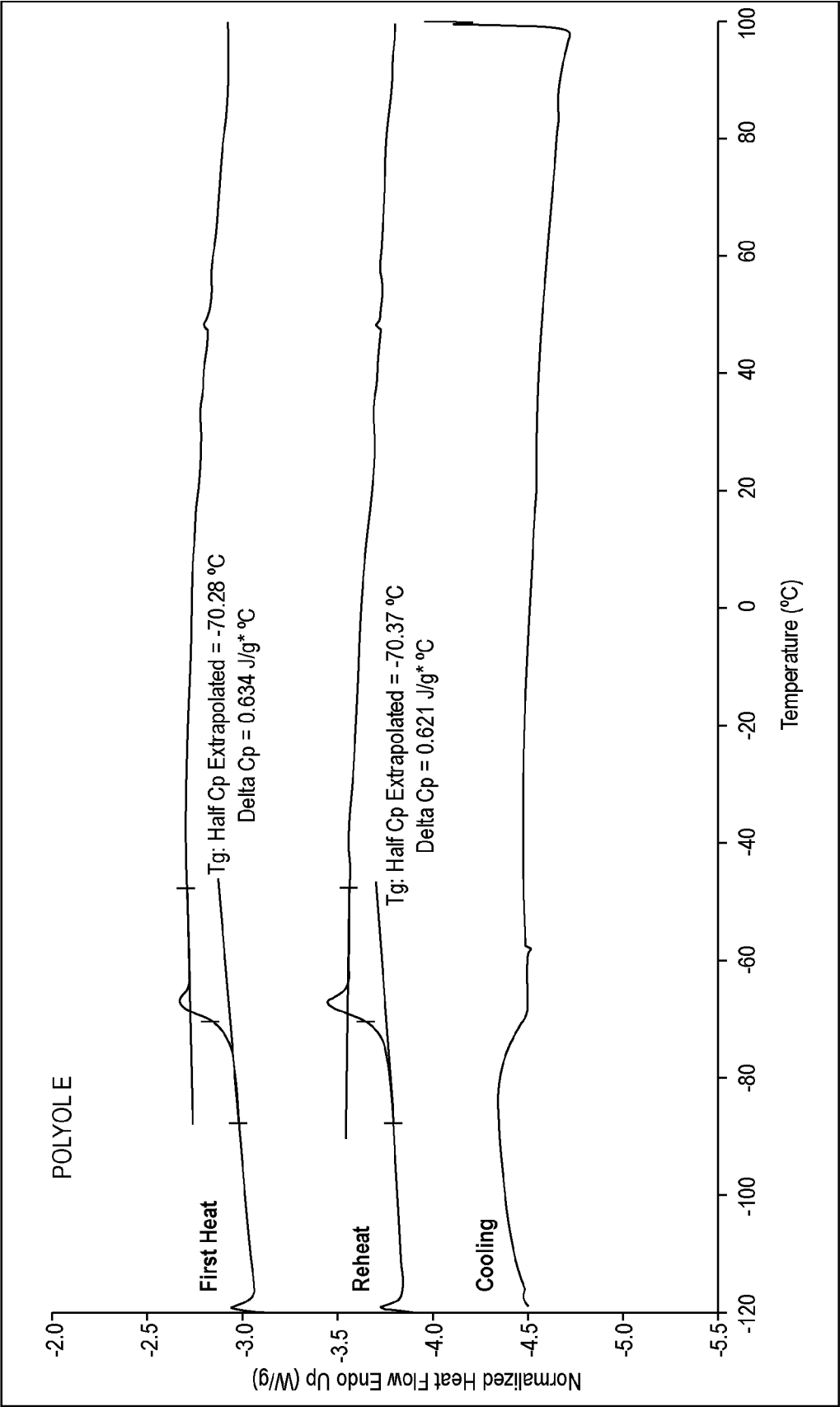


FIG. 5

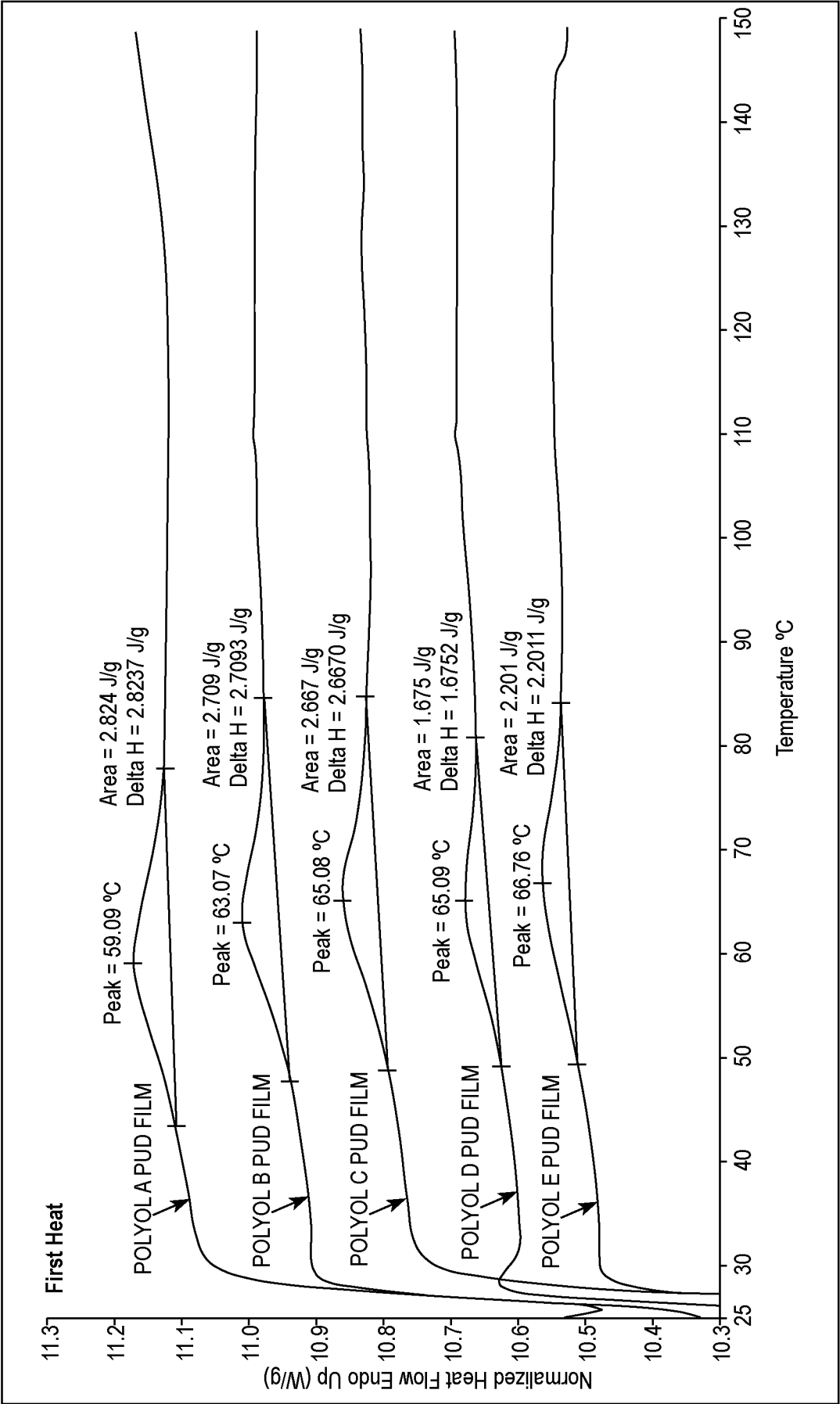


FIG. 6

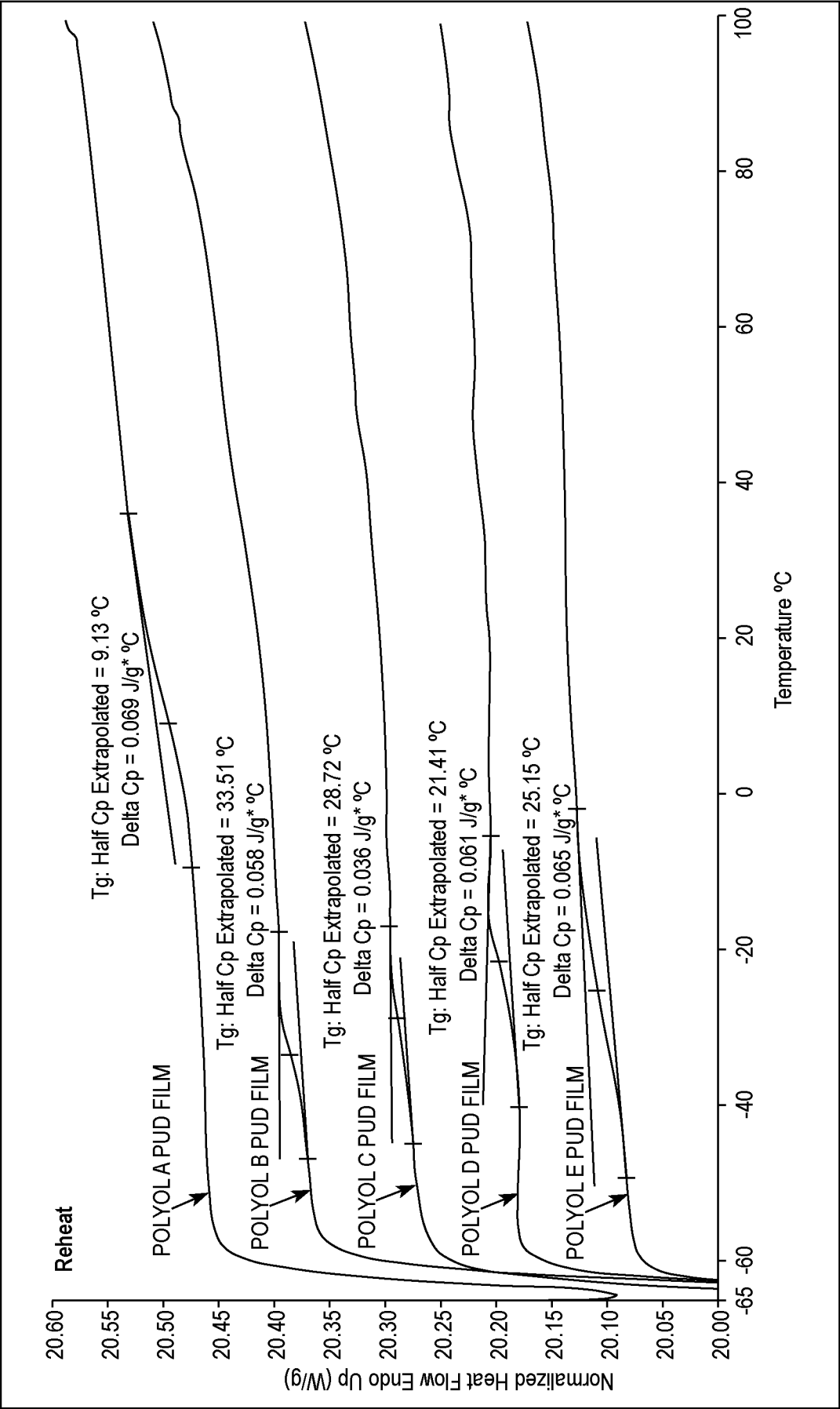


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/044776

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/08 C08G18/65 C08G18/28 C08G18/40
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2015/353771 A1 (KENDI MARGARET A [US]) 10 December 2015 (2015-12-10) paragraph [0001] - paragraph [0112]; claims 5,4,1; example 1; table 9 -----	1-31
A	EP 1 297 047 A2 (OMNOVA SOLUTIONS INC [US]) 2 April 2003 (2003-04-02) page 12, paragraphs 1,81 - page 13, paragraphs 38,86; example 1; table 1 -----	1-31
A	WO 2016/016286 A1 (BASF SE [DE]) 4 February 2016 (2016-02-04) pages 1,16 - pages 1,16 -----	1-31
A	EP 2 921 541 A1 (HENKEL AG & CO KGAA [DE]) 23 September 2015 (2015-09-23) claim 1; example 1 ----- -/-	1-31



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

19 November 2018

Date of mailing of the international search report

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Adigbli, Francis

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/044776

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/158367 A1 (WEINERT RAYMOND J [US] ET AL) 21 August 2003 (2003-08-21) paragraph [0033] - paragraph [0033] -----	1-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/044776

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015353771 A1	10-12-2015	US 2015353771 A1	10-12-2015
		WO 2015191351 A1	17-12-2015

EP 1297047 A2	02-04-2003	AT 345358 T	15-12-2006
		BR 0112219 A	06-05-2003
		DE 60124548 T2	24-05-2007
		EP 1297047 A2	02-04-2003
		JP 2004502844 A	29-01-2004
		MX PA02012667 A	14-05-2003
		US 2002026006 A1	28-02-2002
		WO 0204538 A2	17-01-2002

WO 2016016286 A1	04-02-2016	AR 101399 A1	14-12-2016
		AU 2015295375 A1	02-03-2017
		BR 112017001895 A2	28-11-2017
		CN 106795266 A	31-05-2017
		EP 3174910 A1	07-06-2017
		JP 2017532386 A	02-11-2017
		US 2017226377 A1	10-08-2017
		WO 2016016286 A1	04-02-2016

EP 2921541 A1	23-09-2015	NONE	

US 2003158367 A1	21-08-2003	AT 376013 T	15-11-2007
		CA 2369142 A1	04-01-2001
		DE 60036799 T2	24-07-2008
		EP 1189964 A1	27-03-2002
		JP 2003517504 A	27-05-2003
		US 6673889 B1	06-01-2004
		US 2003158367 A1	21-08-2003
		WO 0100701 A1	04-01-2001
