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(54) Title: INKJET RECEPTIVE THERMOPLASTIC POLYURETHANE FILM

(57) Abstract: The present invention relates to an article useful as a graphic film. The article comprises an ink-receptive layer that is made from a water-swellaible polyurethane resin and an ink layer adjacent to the ink-receptive layer.



INKJET RECEPTIVE THERMOPLASTIC POLYURETHANE FILM

FIELD OF THE INVENTION

[0001] The present relates to an article that that is receptive to inks or dyes. The article comprises a film made from a water-swella-
5 ble polyurethane polymer. In an article, the film is typically used as the outer layer of the article by virtue of its ability to accept ink or dye for labeling and/or ornamental decoration.

BACKGROUND

[0002] Ink receptive films are often used to apply designs, such as graphics or text, onto articles. One area where ink receptive films are useful is printed label stock. Often,
10 ink receptive films comprise a paper or polymeric base layer that is coated with an ink receptive material. Articles having water-based ink-jet receptivity need to aid in dewatering and coagulating the ink in order to minimize surface spreading of the ink, which affects print definition and therefore appearance of the printed article. Often, coatings are applied to the surface of an ink-receptive article. However, it would be useful to provide a poly-
15 meric material that itself is receptive to ink and to form an ink receptive film or article from such polymeric material.

SUMMARY

[0003] The present invention provides an ink receptive article comprising a water-swella-
20 ble polyurethane resin. In one embodiment the water-swella- ble polyurethane resin is a thermoplastic polyurethane composition comprising the reaction product of a hydroxyl-terminated intermediate, a polyisocyanate, and a chain extender. In a preferred embodiment, the thermoplastic polyurethane resin comprises the reaction product of a hydroxyl-terminated intermediate, wherein the hydroxyl terminated intermediate comprises poly(ethylene glycol), a polyisocyanate, and a chain extender. In another embodiment, the
25 thermoplastic polyurethane resin comprises the reaction product of a hydroxyl-terminated intermediate, such as poly(ethylene glycol), an aliphatic diisocyanate, and a chain extender. In one embodiment, the water-swella- ble polyurethane resin has a water absorption range of greater than 60% as measured by ASTM D570. In another embodiment, the water-swella- ble polymer has a water absorption range of about 100% to about 900% as measured
30 by ASTM D570. The ink receptive article may be a film, fabric, or textile product.

[0004] An ink layer may be included on one surface of the ink receptive article. In one embodiment, the ink comprises a water-based ink.

DETAILED DESCRIPTION

[0005] Articles of the present invention may comprise a film, fabric, or textile product comprising a water-swellaable polyurethane resin. In one embodiment, the resin is a thermoplastic polyurethane resin. The water-swellaable polyurethane resin used in the present invention may have a water absorption range of greater than 60%, including greater than 70%, 75%, 80%, 85%, 90%, 95%, and 100%. In some embodiments, the thermoplastic polyurethane resins used in the ink jet receptive articles of the present invention have a water absorption range of from 100% to 900%, as measured by ASTM D570.

[0006] Thermoplastic polyurethane resins are obtained by the reaction of 1) a polyisocyanate, 2) a hydroxyl-functional intermediate, 3) a compound containing a carboxylic group, a sulfonate group, or a phosphate group, either alone or in combination with a hydroxy group, and 4) a chain lengthening reagent. In this reaction, a catalyst is used if needed.

[0007] The polyurethane compositions described herein are made using a polyisocyanate component. The polyisocyanate and/or polyisocyanate component includes one or more polyisocyanates. In some embodiments, the polyisocyanate component includes one or more diisocyanates.

[0008] Examples of useful polyisocyanates include aromatic diisocyanates such as 4,4'-methylenebis(phenyl isocyanate) (MDI), m-xylene diisocyanate (XDI), phenylene-1,4-diisocyanate, naphthalene-1,5-diisocyanate, and toluene diisocyanate (TDI), 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), 1,5-naphthalene diisocyanate (NDI); as well as aliphatic diisocyanates such as isophorone diisocyanate (IPDI), hexamethalyne diisocyanate (HDI), 1,4-cyclohexyl diisocyanate (CHDI), decane-1,10-diisocyanate, lysine diisocyanate (LDI), 1,4-butane diisocyanate (BDI), isophorone diisocyanate (PDI), and dicyclohexylmethane-4,4'-diisocyanate (H12MDI). Mixtures of two or more polyisocyanates may be used. In some embodiments, the polyisocyanate is MDI and/or H12MDI. In some embodiments, the polyisocyanate includes MDI. In some embodiments, the polyisocyanate includes H12MDI. In one useful embodiment, the diisocyanate component consists or consists essentially of an aliphatic diisocyanate.

[0009] The polyurethane resins described herein are also made using a hydroxyl-terminated intermediate component. In one useful embodiment, the hydroxyl-terminated intermediate component comprises a polyol component. Polyols include polyether polyols, polyester polyols, polycarbonate polyols, polysiloxane polyols, and combinations thereof.

5 **[0010]** Suitable polyols, which may also be described as hydroxyl terminated intermediates, when present, may include one or more hydroxyl terminated polyesters, one or more hydroxyl terminated polyethers, one or more hydroxyl terminated polycarbonates, one or more hydroxyl terminated polysiloxanes, or mixtures thereof.

[0011] Suitable hydroxyl terminated polyester intermediates include linear polyesters
10 having a number average molecular weight (Mn) of from about 500 to about 10,000, from about 700 to about 5,000, or from about 700 to about 4,000, and generally have an acid number less than 1.3 or less than 0.5. The molecular weight is determined by assay of the terminal functional groups and is related to the number average molecular weight. The polyester intermediates may be produced by (1) an esterification reaction of one or more
15 glycols with one or more dicarboxylic acids or anhydrides or (2) by transesterification reaction, i.e., the reaction of one or more glycols with esters of dicarboxylic acids. Mole ratios generally in excess of more than one mole of glycol to acid are preferred so as to obtain linear chains having a preponderance of terminal hydroxyl groups. Suitable polyester intermediates also include various lactones such as polycaprolactone typically made
20 from ϵ -caprolactone and a bifunctional initiator such as diethylene glycol. The dicarboxylic acids of the desired polyester can be aliphatic, cycloaliphatic, aromatic, or combinations thereof. Suitable dicarboxylic acids which may be used alone or in mixtures generally have a total of from 4 to 15 carbon atoms and include: succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, isophthalic, terephthalic, cyclohexane dicarboxylic, and the like. Anhydrides of the above dicarboxylic acids such as phthalic anhydride,
25 tetrahydrophthalic anhydride, or the like, can also be used. Adipic acid is a preferred acid. The glycols which are reacted to form a desirable polyester intermediate can be aliphatic, aromatic, or combinations thereof, including any of the glycols described above in the chain extender section, and have a total of from 2 to 20 or from 2 to 12 carbon atoms.
30 Suitable examples include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-

cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and mixtures thereof.

[0012] The polyol component may also include one or more polycaprolactone polyester polyols. The polycaprolactone polyester polyols useful in the technology described herein include polyester diols derived from caprolactone monomers. The polycaprolactone polyester polyols are terminated by primary hydroxyl groups. Suitable polycaprolactone polyester polyols may be made from ϵ -caprolactone and a bifunctional initiator such as diethylene glycol, 1,4-butanediol, or any of the other glycols and/or diols listed herein. In some embodiments, the polycaprolactone polyester polyols are linear polyester diols derived from caprolactone monomers.

[0013] The polycaprolactone polyester polyols may be prepared from 2-oxepanone and a diol, where the diol may be 1,4-butanediol, diethylene glycol, monoethylene glycol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, or any combination thereof. In some embodiments, the diol used to prepare the polycaprolactone polyester polyol is linear. In some embodiments, the polycaprolactone polyester polyol is prepared from 1,4-butanediol. In some embodiments, the polycaprolactone polyester polyol has a number average molecular weight from 500 to 10,000, or from 500 to 5,000, or from 1,000 or even 2,000 to 4,000 or even 3,000.

[0014] Suitable hydroxyl terminated polyether intermediates include polyether polyols derived from a diol or polyol having a total of from 2 to 15 carbon atoms, in some embodiments an alkyl diol or glycol which is reacted with an ether comprising an alkylene oxide having from 2 to 6 carbon atoms, typically ethylene oxide or propylene oxide or mixtures thereof. For example, hydroxyl functional polyether can be produced by first reacting propylene glycol with propylene oxide followed by subsequent reaction with ethylene oxide. Primary hydroxyl groups resulting from ethylene oxide are more reactive than secondary hydroxyl groups and thus are preferred. Useful commercial polyether polyols include poly(ethylene glycol) comprising ethylene oxide reacted with ethylene glycol, poly(propylene glycol) comprising propylene oxide reacted with propylene glycol, poly(tetramethylene ether glycol) comprising water reacted with tetrahydrofuran which can also be described as polymerized tetrahydrofuran, and which is commonly referred to as PTMEG. In some embodiments, the polyether intermediate includes PTMEG. Suitable polyether polyols also include polyamide adducts of an alkylene oxide and can include, for example,

ethylenediamine adduct comprising the reaction product of ethylenediamine and propylene oxide, diethylenetriamine adduct comprising the reaction product of diethylenetriamine with propylene oxide, and similar polyamide type polyether polyols. Copolyethers can also be utilized in the described compositions. Typical copolyethers include the reaction product of THF and ethylene oxide or THF and propylene oxide. The various polyether intermediates, such as poly(ethylene glycol) generally have a number average molecular weight (Mn) as determined by assay of the terminal functional groups which is an average molecular weight greater than about 700, such as from about 700 to about 10,000, from about 1,000 to about 8,000, or from about 1,000 to about 2,500.

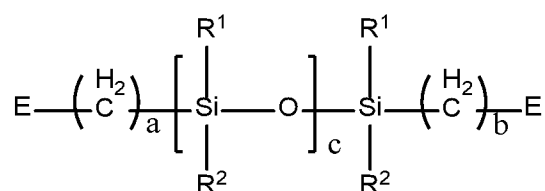
[0015] Suitable hydroxyl terminated polycarbonates include those prepared by reacting a glycol with a carbonate. U.S. Patent No. 4,131,731 is hereby incorporated by reference for its disclosure of hydroxyl terminated polycarbonates and their preparation. Such polycarbonates are linear and have terminal hydroxyl groups with essential exclusion of other terminal groups. The essential reactants are glycols and carbonates. Suitable glycols are selected from cycloaliphatic and aliphatic diols containing 4 to 40, and or even 4 to 12 carbon atoms, and from polyoxyalkylene glycols containing 2 to 20 alkoxy groups per molecule with each alkoxy group containing 2 to 4 carbon atoms. Suitable diols include aliphatic diols containing 4 to 12 carbon atoms such as 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,10-decanediol, hydrogenated dilinoleylglycol, hydrogenated dioleylglycol, 3-methyl-1,5-pentanediol; and cycloaliphatic diols such as 1,3-cyclohexanediol, 1,4-dimethylolcyclohexane, 1,4-cyclohexanediol-, 1,3-dimethylolcyclohexane-, 1,4-endomethylene-2-hydroxy-5-hydroxymethylcyclohexane, and polyalkylene glycols. The diols used in the reaction may be a single diol or a mixture of diols depending on the properties desired in the finished product. Polycarbonate intermediates which are hydroxyl terminated are generally those known to the art and in the literature. Suitable carbonates are selected from alkylene carbonates composed of a 5 to 7 member ring. Suitable carbonates for use herein include ethylene carbonate, trimethylene carbonate, tetramethylene carbonate, 1,2-propylene carbonate, 1,2-butylenecarbonate, 2,3-butylenecarbonate, 1,2-ethylene carbonate, 1,3-pentylene carbonate, 1,4-pentylene carbonate, 2,3-pentylene carbonate, and 2,4-pentylene carbonate. Also, suitable herein are dialkylcarbonates, cycloaliphatic carbonates, and diarylcarbonates. The dialkylcarbonates can contain 2 to 5 carbon atoms in each alkyl group and specific examples

thereof are diethylcarbonate and dipropylcarbonate. Cycloaliphatic carbonates, especially dicycloaliphatic carbonates, can contain 4 to 7 carbon atoms in each cyclic structure, and there can be one or two of such structures. When one group is cycloaliphatic, the other can be either alkyl or aryl. On the other hand, if one group is aryl, the other can be alkyl or cycloaliphatic. Examples of suitable diarylcarbonates, which can contain 6 to 20 carbon atoms in each aryl group, are diphenylcarbonate, ditolylcarbonate, and dinaphthylcarbonate.

[0016] Suitable polysiloxane polyols include α - ω -hydroxyl or amine or carboxylic acid or thiol or epoxy terminated polysiloxanes. Examples include poly(dimethylsiloxane) terminated with a hydroxyl or amine or carboxylic acid or thiol or epoxy group. In some embodiments, the polysiloxane polyols are hydroxyl terminated polysiloxanes. In some embodiments, the polysiloxane polyols have a number-average molecular weight in the range from 300 to 5,000, or from 400 to 3,000.

[0017] Polysiloxane polyols may be obtained by the dehydrogenation reaction between a polysiloxane hydride and an aliphatic polyhydric alcohol or polyoxyalkylene alcohol to introduce the alcoholic hydroxy groups onto the polysiloxane backbone.

[0018] In some embodiments, the polysiloxanes may be represented by one or more compounds having the following formula:



[0019] in which: each R^1 and R^2 are independently a 1 to 4 carbon atom alkyl group, a benzyl, or a phenyl group; each E is OH or NHR^3 where R^3 is hydrogen, a 1 to 6 carbon atoms alkyl group, or a 5 to 8 carbon atoms cyclo-alkyl group; a and b are each independently an integer from 2 to 8; c is an integer from 3 to 50. In amino-containing polysiloxanes, at least one of the E groups is NHR^3 . In the hydroxyl-containing polysiloxanes, at least one of the E groups is OH. In some embodiments, both R^1 and R^2 are methyl groups.

[0020] Suitable examples include α,ω -hydroxypropyl terminated poly(dimethylsiloxane) and α,ω -amino propyl terminated poly(dimethylsiloxane), both of which are commercially available materials. Further examples include copolymers of the poly(dimethylsiloxane) materials with a poly(alkylene oxide).

5 [0021] The polyol component, when present, may include poly(ethylene glycol), poly(tetramethylene ether glycol), poly(trimethylene oxide), ethylene oxide capped poly(propylene glycol), poly(butylene adipate), poly(ethylene adipate), poly(hexamethylene adipate), poly(tetramethylene-co-hexamethylene adipate), poly(3-methyl-1,5-pentamethylene adipate), polycaprolactone diol, poly(hexamethylene carbonate) glycol, 10 poly(pentamethylene carbonate) glycol, poly(trimethylene carbonate) glycol, dimer fatty acid based polyester polyols, vegetable oil based polyols, or any combination thereof.

[0022] Examples of dimer fatty acids that may be used to prepare suitable polyester polyols include Priplast™ polyester glycols/polyols commercially available from Croda and Radia® polyester glycols commercially available from Oleon.

15 [0023] In some embodiments, the polyol component includes a polyether polyol, a polycarbonate polyol, a polycaprolactone polyol, or any combination thereof.

[0024] In some embodiments, the polyol component includes a polyether polyol. In some embodiments, the polyol component is essentially free of or even completely free of polyester polyols. In some embodiments, the polyol component used to prepare the TPU 20 is substantially free of, or even completely free of polysiloxanes.

[0025] In some embodiments, the polyol component includes ethylene oxide, propylene oxide, butylene oxide, styrene oxide, poly(tetramethylene ether glycol), poly(propylene glycol), poly(ethylene glycol), copolymers of poly(ethylene glycol) and poly(propylene glycol), epichlorohydrin, and the like, or combinations thereof. In some embodiments 25 the polyol component includes poly(tetramethylene ether glycol).

[0026] Suitable polyamide oligomers, including telechelic polyamide polyols, are not overly limited and include low molecular weight polyamide oligomers and telechelic polyamides (including copolymers) that include N-alkylated amide groups in the backbone structure. Telechelic polymers are macromolecules that contain two reactive end groups. 30 Amine terminated polyamide oligomers can be useful as polyols in the disclosed technology. The term polyamide oligomer refers to an oligomer with two or more amide linkages,

or sometimes the amount of amide linkages will be specified. A subset of polyamide oligomers are telechelic polyamides. Telechelic polyamides are polyamide oligomers with high percentages, or specified percentages, of two functional groups of a single chemical type, e.g. two terminal amine groups (meaning either primary, secondary, or mixtures), two terminal carboxyl groups, two terminal hydroxyl groups (again meaning primary, secondary, or mixtures), or two terminal isocyanate groups (meaning aliphatic, aromatic, or mixtures). Ranges for the percent difunctional that can meet the definition of telechelic include at least 70, 80, 90 or 95 mole% of the oligomers being difunctional as opposed to higher or lower functionality. Reactive amine terminated telechelic polyamides are telechelic polyamide oligomers where the terminal groups are both amine types, either primary or secondary and mixtures thereof, i.e. excluding tertiary amine groups.

[0027] In one embodiment, the telechelic oligomer or telechelic polyamide will have a viscosity measured by a Brookfield circular disc viscometer with the circular disc spinning at 5 rpm of less than 100,000 cps at a temperature of 70 °C, less than 15,000 or 10,000 cps at 70 °C, less than 100,000 cps at 60 or 50 °C, less than 15,000 or 10,000 cps at 60 °C; or less than 15,000 or 10,000 cps at 50 °C. These viscosities are those of neat telechelic prepolymers or polyamide oligomers without solvent or plasticizers. In some embodiments, the telechelic polyamide can be diluted with solvent to achieve viscosities in these ranges.

[0028] In some embodiments, the polyamide oligomer is a species below 20,000 g/mole molecular weight, e.g. often below 10,000; 5,000; 2,500; or 2,000 g/mole, that has two or more amide linkages per oligomer. The telechelic polyamide has molecular weight preferences identical to the polyamide oligomer. Multiple polyamide oligomers or telechelic polyamides can be linked with condensation reactions to form polymers, generally above 100,000 g/mole.

[0029] Generally amide linkages are formed from the reaction of a carboxylic acid group with an amine group or the ring opening polymerization of a lactam, e.g. where an amide linkage in a ring structure is converted to an amide linkage in a polymer. In one embodiment a large portion of the amine groups of the monomers are secondary amine groups or the nitrogen of the lactam is a tertiary amide group. Secondary amine groups form tertiary amide groups when the amine group reacts with carboxylic acid to form an amide. For the purposes of this disclosure the carbonyl group of an amide, e.g. as in a

lactam, will be considered as derived from a carboxylic acid group. The amide linkage of a lactam is formed from the reaction of carboxylic group of an aminocarboxylic acid with the amine group of the same aminocarboxylic acid. In one embodiment, we want less than 20, 10 or 5 mole percent of the monomers used in making the polyamide to have functionality in polymerization of amide linkages of 3 or more.

[0030] The polyamide oligomers and telechelic polyamides of this disclosure can contain small amounts of ester linkages, ether linkages, urethane linkages, urea linkages, etc. if the additional monomers used to form these linkages are useful to the intended use of the polymers.

[0031] As earlier indicated many amide forming monomers create on average one amide linkage per repeat unit. These include diacids and diamines when reacted with each other, aminocarboxylic acids, and lactams. These monomers, when reacted with other monomers in the same group, also create amide linkages at both ends of the repeat units formed. Thus we will use both percentages of amide linkages and mole percent and weight percentages of repeat units from amide forming monomers. Amide forming monomers will be used to refer to monomers that form on average one amide linkage per repeat unit in normal amide forming condensation linking reactions.

[0032] In one embodiment, at least 10 mole percent, or at least 25, 45 or 50, and or even at least 60, 70, 80, 90, or 95 mole% of the total number of the heteroatom containing linkages connecting hydrocarbon type linkages are characterized as being amide linkages. Heteroatom linkages are linkages such as amide, ester, urethane, urea, ether linkages where a heteroatom connects two portions of an oligomer or polymer that are generally characterized as hydrocarbons (or having carbon to carbon bonds, such as hydrocarbon linkages). As the amount of amide linkages in the polyamide increases, the amount of repeat units from amide forming monomers in the polyamide increases. In one embodiment, at least 25 wt.%, or at least 30, 40, 50, or even at least 60, 70, 80, 90, or 95 wt.% of the polyamide oligomer or telechelic polyamide is repeat units from amide forming monomers, also identified as monomers that form amide linkages at both ends of the repeat unit. Such monomers include lactams, aminocarboxylic acids, dicarboxylic acid and diamines. In one embodiment, at least 50, 65, 75, 76, 80, 90, or 95 mole percent of the amide linkages in the polyamide oligomer or telechelic polyamine are tertiary amide linkages.

[0033] The percent of tertiary amide linkages of the total number of amide linkages was calculated with the following equation:

$$\text{Tertiary amide linkage \%} = \frac{\sum_{i=1}^n (w_{tertN,i} \times n_i)}{\sum_{i=1}^n (w_{totalN,i} \times n_i)} \times 100$$

5 where: n is the number of monomers; the index i refers to a certain monomer; w_{tertN} is the average number nitrogen atoms in a monomer that form or are part of tertiary amide linkages in the polymerizations, (note: end-group forming amines do not form amide groups during the polymerizations and their amounts are excluded from w_{tertN}); w_{totalN} is the average number nitrogen atoms in a monomer that form or are part of tertiary amide linkages
10 in the polymerizations (note: the end-group forming amines do not form amide groups during the polymerizations and their amounts are excluded from w_{totalN}); and n_i is the number of moles of the monomer with the index i .

[0034] The percent of amide linkages of the total number of all heteroatom containing linkages (connecting hydrocarbon linkages) was calculated by the following equation:

$$15 \quad \text{Amide linkage \%} = \frac{\sum_{i=1}^n (w_{totalN,i} \times n_i)}{\sum_{i=1}^n (w_{totalS,i} \times n_i)} \times 100$$

where: w_{totalS} is the sum of the average number of heteroatom containing linkages (connecting hydrocarbon linkages) in a monomer and the number of heteroatom containing linkages (connecting hydrocarbon linkages) forming from that monomer by the reaction
20 with a carboxylic acid bearing monomer during the polyamide polymerizations; and all other variables are as defined above. The term “hydrocarbon linkages” as used herein are just the hydrocarbon portion of each repeat unit formed from continuous carbon to carbon bonds (i.e. without heteroatoms such as nitrogen or oxygen) in a repeat unit. This hydrocarbon portion would be the ethylene or propylene portion of ethylene oxide or propylene
25 oxide; the undecyl group of dodecyl lactam, the ethylene group of ethylenediamine, and the $(CH_2)_4$ (or butylene) group of adipic acid.

[0035] In some embodiments, the amide or tertiary amide forming monomers include dicarboxylic acids, diamines, aminocarboxylic acids and lactams. Suitable dicarboxylic acids are where the alkylene portion of the dicarboxylic acid is a cyclic, linear, or branched

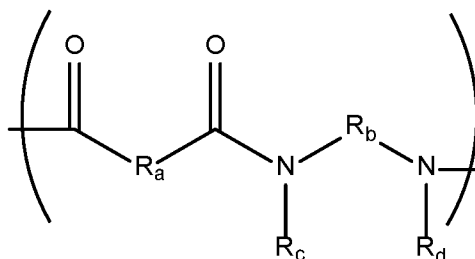
(optionally including aromatic groups) alkylene of 2 to 36 carbon atoms, optionally including up to 1 heteroatom per 3 or 10 carbon atoms of the diacid, more preferably from 4 to 36 carbon atoms (the diacid would include 2 more carbon atoms than the alkylene portion). These include dimer fatty acids, hydrogenated dimer acid, sebacic acid, etc.

5 **[0036]** Suitable diamines include those with up to 60 carbon atoms, optionally including one heteroatom (besides the two nitrogen atoms) for each 3 or 10 carbon atoms of the diamine and optionally including a variety of cyclic, aromatic or heterocyclic groups providing that one or both of the amine groups are secondary amines.

10 **[0037]** Such diamines include EthacureTM 90 from Albermarle (supposedly a N,N'-bis(1,2,2-trimethylpropyl)- 1,6-hexanediamine); ClearlinkTM 1000 from Dorf Ketal, or JefflinkTM 754 from Huntsman; N-methylaminoethanol; dihydroxy terminated, hydroxyl and amine terminated or diamine terminated poly(alkyleneoxide) where the alkylene has from 2 to 4 carbon atoms and having molecular weights from about 40 or 100 to 2,000; N,N'-diisopropyl-1,6-hexanediamine; N,N'-di(sec-butyl) phenylenediamine; piperazine;
15 homopiperazine; and methyl-piperazine.

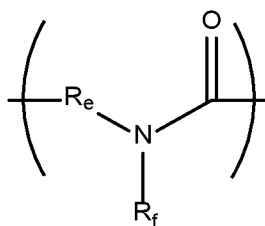
20 **[0038]** Suitable lactams include straight chain or branched alkylene segments therein of 4 to 12 carbon atoms such that the ring structure without substituents on the nitrogen of the lactam has 5 to 13 carbon atoms total (when one includes the carbonyl) and the substituent on the nitrogen of the lactam (if the lactam is a tertiary amide) is an alkyl group of
25 from 1 to 8 carbon atoms and more desirably an alkyl group of 1 to 4 carbon atoms. Dodecyl lactam, alkyl substituted dodecyl lactam, caprolactam, alkyl substituted caprolactam, and other lactams with larger alkylene groups are preferred lactams as they provide repeat units with lower Tg values. Aminocarboxylic acids have the same number of carbon atoms as the lactams. In some embodiments, the number of carbon atoms in the linear or branched
30 alkylene group between the amine and carboxylic acid group of the aminocarboxylic acid is from 4 to 12 and the substituent on the nitrogen of the amine group (if it is a secondary amine group) is an alkyl group with from 1 to 8 carbon atoms, or from 1 or 2 to 4 carbon atoms.

35 **[0039]** In one embodiment, desirably at least 50 wt.%, or at least 60, 70, 80 or 90 wt.% of said polyamide oligomer or telechelic polyamide comprise repeat units from diacids and diamines of the structure of the repeat unit being:



wherein: R_a is the alkylene portion of the dicarboxylic acid and is a cyclic, linear, or branched (optionally including aromatic groups) alkylene of 2 to 36 carbon atoms, optionally including up to 1 heteroatom per 3 or 10 carbon atoms of the diacid, more preferably from 4 to 36 carbon atoms (the diacid would include 2 more carbon atoms than the alkylene portion); and R_b is a direct bond or a linear or branched (optionally being or including cyclic, heterocyclic, or aromatic portion(s)) alkylene group (optionally containing up to 1 or 3 heteroatoms per 10 carbon atoms) of 2 to 36 or 60 carbon atoms and more preferably 2 or 4 to 12 carbon atoms and R_c and R_d are individually a linear or branched alkyl group of 1 to 8 carbon atoms, more preferably 1 or 2 to 4 carbon atoms or R_c and R_d connect together to form a single linear or branched alkylene group of 1 to 8 carbon atoms or optionally with one of R_c and R_d is connected to R_b at a carbon atom, more desirably R_c and R_d being an alkyl group of 1 or 2 to 4 carbon atoms.

[0040] In one embodiment, desirably at least 50 wt.%, or at least 60, 70, 80 or 90 wt.% of said polyamide oligomer or telechelic polyamide comprise repeat units from lactams or amino carboxylic acids of the structure:



Repeat units can be in a variety of orientations in the oligomer derived from lactams or amino carboxylic acid depending on initiator type, wherein each R_e independently is linear or branched alkylene of 4 to 12 carbon atoms and each R_f independently is a linear or branched alkyl of 1 to 8, more desirably 1 or 2 to 4, carbon atoms.

[0041] In some embodiments, the telechelic polyamide polyols include those having (i) repeat units derived from polymerizing monomers connected by linkages between the repeat units and functional end groups selected from carboxyl or primary or secondary amine, wherein at least 70 mole percent of telechelic polyamide have exactly two functional end groups of the same functional type selected from the group consisting of amino or carboxylic end groups; (ii) a polyamide segment comprising at least two amide linkages characterized as being derived from reacting an amine with a carboxyl group, and said polyamide segment comprising repeat units derived from polymerizing two or more of monomers selected from lactams, aminocarboxylic acids, dicarboxylic acids, and diamines; (iii) wherein at least 10 percent of the total number of the heteroatom containing linkages connecting hydrocarbon type linkages are characterized as being amide linkages; and (iv) wherein at least 25 percent of the amide linkages are characterized as being tertiary amide linkages.

[0042] The TPU compositions described herein are made using c) a chain extender component. Chain extenders include diols, diamines, and combination thereof.

[0043] Suitable chain extenders include relatively small polyhydroxy compounds, for example lower aliphatic or short chain glycols having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms. Suitable examples include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol (BDO), 1,6-hexanediol (HDO), 1,3-butanediol, 1,5-pentanediol, neopentylglycol, 1,4-cyclohexanedimethanol (CHDM), 2,2-bis[4-(2-hydroxyethoxy) phenyl]propane (HEPP), hexamethylenediol, heptanediol, nonanediol, dodecanediol, 3-methyl-1,5-pentanediol, ethylenediamine, butanediamine, hexamethylenediamine, and hydroxyethyl resorcinol (HER), and the like, as well as mixtures thereof. In some embodiments the chain extender includes BDO, HDO, 3-methyl-1,5-pentanediol, or a combination thereof. In some embodiments, the chain extender includes BDO.

[0044] The three reactants (the polyol intermediate, the diisocyanate, and the chain extender) may be reacted together to form the TPU useful in this invention. Any known processes to react the three reactants may be used to make the TPU. The polyol intermediate component of the thermoplastic polyurethane composition is sometimes referred to as the “soft-segment” while the combination of the diisocyanate component and chain extender are referred to as the “hard-segment”. In a preferred embodiment, the hydroxyl-terminated intermediate used for preparing the thermoplastic polyurethane composition

comprises poly(ethylene glycol). In one embodiment, the hydroxyl-terminated intermediate used for preparing the thermoplastic polyurethane composition consists essentially of or even consists of poly(ethylene glycol). In another embodiment, the inkjet receptive article of the present invention comprises a thermoplastic polyurethane composition comprising at least about 59% by weight poly(ethylene glycol). In some embodiments, the inkjet receptive article of the present invention comprises a thermoplastic polyurethane composition comprising the reaction product of a hydroxyl-terminated intermediate which comprises or consists of poly(ethylene glycol), an aliphatic diisocyanate, and a chain extender. In some embodiments, the amount of poly(ethylene glycol) used in the composition will depend on various factors understood by those of ordinary skill in the art, including the molecular weight of the poly(ethylene glycol) and the presence of other polyols in the reaction mixture. In other exemplary embodiments, the inkjet receptive article of the present invention comprises a thermoplastic polyurethane comprising 40% by weight or less of hard segment.

[0045] In one embodiment, the process for making a thermoplastic polyurethane composition as used in the invention herein is a so-called “one-shot” process where all three reactants are added to an extruder reactor and reacted. The equivalent weight amount of the diisocyanate to the total equivalent weight amount of the hydroxyl containing components, that is, the polyol intermediate and the chain extender glycol, can be from about 0.95 to about 1.10, or from about 0.96 to about 1.02, and even from about 0.97 to about 1.005. Reaction temperatures utilizing a urethane catalyst can be from about 175 to about 245 °C, and in another embodiment from 180 to 220 °C.

[0046] The TPU can also be prepared utilizing a pre-polymer process. In the pre-polymer route, the polyol intermediates are reacted with generally an equivalent excess of one or more diisocyanates to form a pre-polymer solution having free or unreacted diisocyanate therein. The reaction is generally carried out at temperatures of from about 80 to about 220 °C, or from about 150 to about 200 °C in the presence of a suitable urethane catalyst. Subsequently, a chain extender, as noted above, is added in an equivalent amount generally equal to the isocyanate end groups as well as to any free or unreacted diisocyanate compounds. The overall equivalent ratio of the total diisocyanate to the total equivalent of the polyol intermediate and the chain extender is thus from about 0.95 to about 1.10, or from about 0.96 to about 1.02 and even from about 0.97 to about 1.05. The chain extension

reaction temperature is generally from about 180 to about 250 °C or from about 200 to about 240 °C. Typically, the pre-polymer route can be carried out in any conventional device including an extruder. In such embodiments, the polyol intermediates are reacted with an equivalent excess of a diisocyanate in a first portion of the extruder to form a pre-polymer solution and subsequently the chain extender is added at a downstream portion and reacted with the pre-polymer solution. Any conventional extruder can be utilized, including extruders equipped with barrier screws having a length to diameter ratio of at least 20 and in some embodiments at least 25.

[0047] In one embodiment, the ingredients are mixed on a single or twin screw extruder with multiple heat zones and multiple feed ports between its feed end and its die end. The ingredients may be added at one or more of the feed ports and the resulting TPU composition that exits the die end of the extruder may be pelletized.

[0048] The preparation of the various polyurethanes in accordance with conventional procedures and methods and since as noted above, generally any type of polyurethane can be utilized, the various amounts of specific components thereof, the various reactant ratios, processing temperatures, catalysts in the amount thereof, polymerizing equipment such as the various types of extruders, and the like, are all generally conventional, and well as known to the art and to the literature.

[0049] The described process for preparing the TPU of the invention includes both the “pre-polymer” process and the “one shot” process, in either a batch or continuous manner. That is, in some embodiments the TPU may be made by reacting the components together in a “one shot” polymerization process wherein all of the components, including reactants are added together simultaneously or substantially simultaneously to a heated extruder and reacted to form the TPU. While in other embodiments the TPU may be made by first reacting the polyisocyanate component with some portion of the polyol component forming a pre-polymer, and then completing the reaction by reacting the pre-polymer with the remaining reactants, resulting in the TPU.

[0050] After exiting the extruder, the composition is normally pelletized and stored in moisture proof packaging and is ultimately sold in pellet form. It being understood that the composition would not always need to be pelletized, but rather could be extruded directly from the reaction extruder through a die into a final product profile.

[0051] One or more polymerization catalysts may be present during the polymerization reaction. Generally, any conventional catalyst can be utilized to react the diisocyanate with the polyol intermediates or the chain extender. Examples of suitable catalysts which in particular accelerate the reaction between the NCO groups of the diisocyanates and the hydroxy groups of the polyols and chain extenders are the conventional tertiary amines known from the prior art, e.g. triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylaminoethoxy)ethanol, diazabicyclo[2.2.2]octane and the like, and also in particular organometallic compounds, such as titanate esters, iron compounds, e.g. ferric acetylacetonate, tin compounds, e.g. stannous diacetate, stannous dioctoate, stannous dilaurate, or the dialkyltin salts of aliphatic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, or the like. The amounts usually used of the catalysts are from 0.0001 to 0.1 part by weight per 100 parts by weight of polyhydroxy compound (b).

[0052] Various types of optional components can be present during the polymerization reaction, and/or incorporated into the TPU elastomer described above to improve processing and other properties. These additives include but are not limited to antioxidants, such as phenolic types, organic phosphites, phosphines and phosphonites, hindered amines, organic amines, organo sulfur compounds, lactones and hydroxylamine compounds, biocides, fungicides, antimicrobial agents, compatibilizers, electro-dissipative or anti-static additives, fillers and reinforcing agents, such as titanium dioxide, alumina, clay and carbon black, flame retardants, such as phosphates, halogenated materials, and metal salts of alkyl benzenesulfonates, impact modifiers, such as methacrylate-butadiene-styrene ("MBS") and methylmethacrylate butylacrylate ("MBA"), mold release agents such as waxes, fats and oils, pigments and colorants, plasticizers, polymers, rheology modifiers such as monoamines, polyamide waxes, silicones, and polysiloxanes, slip additives, such as paraffinic waxes, hydrocarbon polyolefins and/or fluorinated polyolefins, and UV stabilizers, which may be of the hindered amine light stabilizers (HALS) and/or UV light absorber (UVA) types. Other additives may be used to enhance the performance of the TPU composition or blended product. All of the additives described above may be used in an effective amount customary for these substances.

[0053] Pigments or fillers may be used to modify the optical properties of the film such as color, opacity and to improve UV weathering resistance. Suitable pigments and fillers

include, for instance, titanium dioxide, carbon black, zinc oxide, calcium carbonate, silicates, silico-aluminates, antimony trioxide, mica, graphite, talc and other similar mineral fillers, ceramic microspheres, glass or polymeric beads or bubbles, metal particles, fibers, or starch or any other commercially available pigments or fillers. If included, pigments or fillers may be used in amounts from about 0.5% up to about 40% by weight of the total film weight of the ink-receptive layer.

[0054] Other additives may be compounded into a polyurethane composition in order to aid the ink receptivity of the article. For instance, coagulative species or cationic species, such as calcium or aluminum chloride can be compounded into the film. Without being limited to any particular theory, because many ink-jet inks are anionic in nature incorporating a cationic species into the film may aid in coagulating the ink on the film. Cationic species such as metal salts, including but not limited to calcium chloride, calcium nitride, and calcium acetate can be polymerized into the backbone of the thermoplastic polyurethane composition. Other cationic species may be added to the thermoplastic polyurethane when it is extruded into a film. In one embodiment, porous silica or other porous additives may be compounded into the film to provide a diffusion path to rapidly channel ink carrier fluid water content away from the printed surface. In some embodiments, the water-swella- ble polyurethane polymer of the present invention can provide an ink-jet receptive surface that provides good print quality and quick ink drying without the need for coagulating additives such as calcium or aluminum chloride, or porous additives, such as silica or alu- minum oxide. In one embodiment, the ink jet receptive article includes an ink receptive layer comprising a thermoplastic polyurethane extruded film wherein the ink receptive layer is substantially free or completely free of coagulating additives and/or porous addi- tives.

[0055] Preferably, the ink receptive layer is made from a material that is substantially free of additives or components that will interfere with the surface wettability of the ink receptive layer. Such materials include any materials which may change the lower the sur- face energy of the ink receptive layer, such as waxes, silicone or fluorine based species, anti-foaming agents, and lubricants. In one embodiment, the ink receptive layer is substan- tially free of wax, silicone or fluorine species, anti-foam agents, and lubricants.

[0056] These additional additives can be incorporated into the components of, or into the reaction mixture for, the preparation of the TPU resin, or after making the TPU resin.

In another process, all the materials can be mixed with the TPU resin and then melted or they can be incorporated directly into the melt of the TPU resin.

[0057] TPU resins of the present invention preferably are water swellable. In one embodiment, the water swellable thermoplastic polyurethane resins have a water absorption range of at least about 40% as measured by ASTM D570. In another embodiment, the water swellable thermoplastic polyurethane resins have a water absorption range of greater than 100%, or even 100% to 900% as measured by ASTM D570.

[0058] The compositions of the invention and any blends thereof may be formed into monolayer or multilayer films, including breathable films. These films may be formed by any of the conventional techniques known in the art including extrusion, co-extrusion, extrusion coating, lamination, blowing and casting or any combination thereof. The film may be obtained by the flat film or tubular process which may be followed by orientation in a uniaxial direction or in two mutually perpendicular directions in the plane of the film. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. This orientation may occur before or after the individual layers are brought together. Typically, the films are oriented in the Machine Direction (MD) at a ratio of up to 15, preferably between 5 and 7, and in the Transverse Direction (TD) at a ratio of up to 15 preferably 7 to 9. However in another embodiment, the film is oriented to the same extent in both the MD and TD directions.

[0059] The invention further provides for an article, such as a fabric or textile, where the article comprises fibers and the thermoplastic polyurethane composition described herein is included in the fibers. That is the invention provides for a fiber, as well as articles made from such a fiber, where the fiber includes (i.e. is made from) the thermoplastic polyurethane composition described herein. In some embodiments, the fiber may include a monofilament fiber or multifilament fiber. In some embodiments, the fiber is formed by melt blowing, spunbonding, film aperturing, staple fiber carding, continuous filament spinning, or bulked continuous filament spinning.

[0060] Fibers made from the thermoplastic polyurethane composition described herein, in particular, a thermoplastic polyurethane composition having a water absorption range of greater than 60% as measured by ASTM D570, may be used to make fabrics or textile products. For example, a fiber may be spun from a thermoplastic polyurethane composition comprising a hydroxyl-terminated intermediate, such as poly(ethylene glycol), an

aliphatic diisocyanate, and a chain extender, wherein the thermoplastic polyurethane has a water absorption range of greater than 60%, or even 100% to 900% as measured by ASTM D570. Such a fiber may be used to make fabrics or textiles that may be used as an ink receptive layer in an ink jet receptive article as described herein.

5 **[0061]** In one embodiment, ink-jet receptive articles of the present invention may have a multi-layer film construction. In such an embodiment, film layers may be made of different polymer materials or the same polymer material with different additives or different additive blends. One or more additional film layers may be included in the ink-jet receptive article. The one or more additional film layers may comprise other polymers, including
10 but not limited to non-swellable thermoplastic polyurethane polymers, styrene polymers, polyester polymers, polyolefin polymers, polyamide polymers, and polyvinyl chloride polymers. In addition, the ink-jet receptive articles of the present invention may include one or more non-polymeric layers, such as paper, or glass.

15 **[0062]** In some embodiments, an adhesive layer may be applied to a surface of the film. The adhesive layer may be activated by pressure, heat, solvent or any combination thereof and may be of any type useful for the article of the present invention. Exemplary adhesives may include poly- α -olefin, block copolymers, acrylates, natural or synthetic rubbers or resins, or silicones. Pressure-sensitive adhesives may also be used. If included, an adhesive layer may be applied using any conventional technique known to those skilled in
20 the art. For example, the adhesive layer may be applied by roll coating or extrusion coating. The adhesive may also be applied by laminating the film with an adhesive layer with an optional release liner. In some embodiments, the adhesive layer is a repositionable adhesive layer, such that the adhesive layer may be repeatedly adhered to and removed from a substrate without substantial loss of adhesion. The adhesive layer may be useful to adhere
25 one layer of the ink-receptive article to another layer or to adhere the ink-receptive article to a substrate.

30 **[0063]** The ink-jet receptive article of the present invention is particularly useful as a graphic film. The present invention also provides a method of providing a graphic film with a design imaged on the graphic film wherein the article comprises a film layer comprising a water-swellable polyurethane resin and an ink layer on at least one surface of the ink-receptive layer. The method includes securing the graphic film to a substrate.

[0064] Imaging techniques suitable for imaging the film include ink jet printing or other printing processes that used water-based inks. It should be noted that the term “water-based ink” does not require that the ink composition includes water as the majority component. Other components and carrier fluids may be present provided that water is included in the ink composition. Useful inks include piezo ink-jet inks, ultra violet curable inks, and latex inks.

[0065] EXAMPLES

[0066] A set of thermoplastic polyurethane compositions were prepared and the water absorption properties measured. The thermoplastic polyurethane compositions are listed below in Table 1 (%Swell is a measure of water absorption range using ASTM D570). Examples C1 and C2 are comparative, while Examples 3-6 are inventive.

Table 1

	Ex. C1	Ex. C2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
PEG Type	PEG 1000 Mn	PEG 1450 Mn	PEG 1450 Mn	PEG 1450 Mn	PEG 8000 Mn	PEG 8000 Mn
PEG Content (Wt. %)	48	56	59	70	82	90
Isocyanate	MDI	MDI	H12MDI	H12MDI	H12MDI	H12MDI
Hard Segment (Wt. %)	52	44	40	40	17	10
% Swell	40	60	100	150	500	900

[0067] The TPU compositions from Table 1 were used to make an ink-receptive film of the thickness indicated. The quality of the printing using an Epson C88 printer using Epson DuraBrite™ pigment water based ink was evaluated by observing the film physical attributes, ink drying rate, image quality, and wet finger rub of the ink. The results for various thermoplastic polyurethane compositions is summarized in Table 2.

Table 2

Ex.	Thick-ness (mil)	Film Property			Printing Property		
		Transparent	Color	Hand feel	Ink Drying ¹	Wet Finger Rub ²	Image Quality Observation
Plain paper							Good image quality, no ink mottle and no color to color ink bleed, dull image
C1	1	Yes	Clear	Soft, tacky	Very slow	Black rubs off	Mottled, a lot of color to color bleeding
	3	Yes	Clear	Soft, tacky	Very slow	Black rubs off	Mottled, a lot of color to color bleeding
C2	1	Yes	Clear	Soft, tacky	Very slow	Black rubs off, color stays	Mottled, color to color bleeding
	3	Yes	Clear	Soft, tacky	Very slow	Black rubs off, color stays	Mottled, color to color bleeding
3	1	Yes	Clear	Soft, smooth	Fair ink dry	Black rubs off, color stays	Bleed and mottle is a little worse than those of 3 mil sample
	3	Yes	Clear	Soft, smooth	Fair ink dry	Black rubs off, color stays	Some color to color bleed and ink mottle, great color densities
4	1	Yes	Clear	Soft, tacky	Good ink dry	Black rubs off, color stays	Slight color to color bleed and ink mottle, great color densities
	3	Yes	Clear	Soft, tacky	Good ink dry	Black rubs off, color stays	Slight color to color bleed and ink mottle, great color densities
5	1	Translucent	Foggy	Soft	Fast	Good ink rub off	Good image quality, low ink gloss, sharp line, good ink densities
	3	Translucent	Foggy	Soft	Fast	Good ink rub off	Good image quality, low ink gloss, sharp line, good ink densities
6	1	Translucent	Foggy	Soft	Fast	Ink rubs off, tacky wet film	Excellent image quality, no bleeds, low ink gloss, sharp lines

	3	Translucent	Foggy	Soft	Fast	Ink rubs off, tacky wet film	Excellent image quality, no bleeds, low ink gloss, sharp lines
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¹ Ink drying rate was measured by printing a standard test pattern and placing a sheet of white paper over the color bars in the printed image and pressing with a 5lb roller to ensure contact between the paper and the printed image. The imprinting from the printed image to the paper was used to judge the ink drying speed. The longer the imprinting due to wet ink transfer, the slower the ink drying. “Good” indicates that only about 1/8 of the color bars imprinted on the paper. “Fair” indicates that there was imprinting of about 1/4 of the color bars. “Slow” indicates there was about 1/2 of the color bars imprinted on the paper. “Very Slow” indicates that the full color bars imprinted on the paper.

² The Wet Finger Rub test involved rubbing a water moistened index finger across the color bars and observing the ink. “Good ink rub off” indicates that very little of the ink was rubbed off. “Black rubs off” indicates that black ink was rubbed off easily. “Color stays” indicates that colored inks (not black) stayed with rubbing.

[0068] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word “about”. Except where otherwise indicated, all numerical quantities in the description specifying amounts or ratios of materials are on a weight basis. Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression “consisting essentially of” permits the inclusion of substances that do not materially affect the basic and novel characteristics of

the composition under consideration. In addition, as used herein, the expression, “substantially free of” means an amount that does not materially affect the basic and novel characteristics of the composition under consideration, for example, in some embodiments, it may mean no more than 5%, 4%, 3%, 2%, 1%, 0.5%, or even 0.1% by weight of the composition in question, in still other embodiments, it may mean that less than 1,000 ppm, 500 ppm, or even 100 ppm of the material in question is present.

Claims

What is claimed is:

1. An inkjet receptive article, comprising:

an ink receptive layer comprising a water swellable polyurethane resin, wherein the polyurethane resin has a water absorption range of greater than 60% as measured by ASTM D570.

2. The inkjet receptive article of claim 1 wherein the water swellable polymer is a thermoplastic polyurethane polymer comprising the reaction product of a hydroxyl-terminated intermediate comprising poly(ethylene glycol), a polyisocyanate, and a chain extender, wherein the polyisocyanate and the chain extender form a hard segment of the polymer.

3. The inkjet receptive article of claim 1 wherein the water swellable polymer is a thermoplastic polyurethane polymer comprising the reaction product of a hydroxyl terminated intermediate comprising poly(ethylene glycol), an aliphatic polyisocyanate, and a chain extender, wherein the polyisocyanate and the chain extender form a hard segment of the polymer.

4. The inkjet receptive article of any of claims 2 or 3 wherein the water swellable polymer includes 40% by weight or less hard segment.

5. The inkjet receptive article of any of claims 2 to 4 wherein the water swellable polymer includes at least 50% by weight poly(ethylene glycol).

6. The inject receptive article of any of claims 1 to 6 wherein the thermoplastic polyurethane polymer has a water absorption range of about 100% to about 900% as measured by ASTM D570.

7. The inkjet receptive article of any of claims 1 to 7 further comprising additives selected from silicas, coagulants, and fillers.

8. The inkjet receptive article of any of claims 1 to 7 wherein the ink receptive layer is cationic.

5 9. The inkjet receptive article of any of claims 1 to 8 wherein the inkjet receptive layer is an extruded film.

10. The inkjet receptive article of any of claims 1 to 9 wherein the inkjet receptive layer is a fabric.

10 11. The inkjet receptive article of any of claims 1 to 10 wherein the inkjet receptive layer is a textile product.

12. The inkjet receptive article of any of claims 1 to 11 further comprising an ink layer adjacent to at least one surface of the ink receptive layer.

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13. The inkjet receptive article of any of claims 1 to 11 wherein the inkjet receptive article further comprises one or more additional layers, wherein the one or more additional layers comprise polymers selected from the group consisting of non-swellable thermoplastic polyurethane polymers, styrene polymers, polyester polymers, polyolefin polymers, polyamide polymers, and polyvinyl chloride polymers.

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14. An inkjet receptive article comprising:
an ink receptive layer consisting essentially of a water swellable thermoplastic polyurethane polymer extruded film.

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15. The inkjet receptive article of claim 14 wherein the water swellable thermoplastic polyurethane comprises the reaction product of a hydroxyl-terminated intermediate, a polyisocyanate, and a chain extender, wherein the hydroxyl-terminated intermediate comprises poly(ethylene glycol).

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16. The inkjet receptive article of claim 15 wherein the polyisocyanate comprises an aliphatic polyisocyanate.

17. A printed article comprising:
an inkjet receptive surface, said inkjet receptive surface formed from a water-sw
5 swellable polyurethane polymer; and
a water-based ink.

18. The printed article of claim 17, wherein the water swellable thermoplastic polyu-
rethane comprises the reaction product of a hydroxyl-terminated intermediate, a polyiso-
cyanate, and a chain extender, wherein the hydroxyl-terminated intermediate comprises
10 poly(ethylene glycol).

19. The printed article of claim 17, wherein the polyisocyanate comprises an aliphatic
polyisocyanate.

15 20. The printed article of claim 17 wherein the water-based ink comprises a dye.

21. The printed article of claim 17 wherein the water-based ink comprises a pigment.

22. A multi-layer printed article comprising:
20 an inkjet receptive layer comprising a water-swallowable thermoplastic polyurethane
polymer; and
a water based ink.

23. The multi-layer printed article of claim 22 wherein the water swellable thermo-
25 plastic polyurethane comprises the reaction product of a hydroxyl-terminated intermedi-
ate, a polyisocyanate, and a chain extender, wherein the hydroxyl-terminated intermediate
comprises poly(ethylene glycol).

24. The multi-layer printed article of claim 22 wherein the polyisocyanate comprises
30 an aliphatic polyisocyanate.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/038079

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G18/48 B41M1/30 C08G18/75 C08J5/18 B41M5/52 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 B41M C08J																	
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 <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>JP 2004 025534 A (OKADA ENGINEERING KK) 29 January 2004 (2004-01-29) claim 1; examples 1-4 -----</td> <td>1-24</td> </tr> <tr> <td>X</td> <td>EP 0 858 904 A1 (DAINICHISEIKA COLOR CHEM [JP]; UKIMA COLOUR & CHEM MFG [JP]) 19 August 1998 (1998-08-19) page 2, lines 7-10; example 5 -----</td> <td>1-24</td> </tr> <tr> <td>X</td> <td>JP 2002 067484 A (OKADA ENGINEERING KK) 5 March 2002 (2002-03-05) claim 1; example 1 -----</td> <td>1-24</td> </tr> <tr> <td>X</td> <td>JP 2001 071630 A (NIPPON MEKTRON KK; OKADA ENGINEERING KK) 21 March 2001 (2001-03-21) example 1 ----- -/-</td> <td>1-24</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	JP 2004 025534 A (OKADA ENGINEERING KK) 29 January 2004 (2004-01-29) claim 1; examples 1-4 -----	1-24	X	EP 0 858 904 A1 (DAINICHISEIKA COLOR CHEM [JP]; UKIMA COLOUR & CHEM MFG [JP]) 19 August 1998 (1998-08-19) page 2, lines 7-10; example 5 -----	1-24	X	JP 2002 067484 A (OKADA ENGINEERING KK) 5 March 2002 (2002-03-05) claim 1; example 1 -----	1-24	X	JP 2001 071630 A (NIPPON MEKTRON KK; OKADA ENGINEERING KK) 21 March 2001 (2001-03-21) example 1 ----- -/-	1-24
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X	JP 2001 071630 A (NIPPON MEKTRON KK; OKADA ENGINEERING KK) 21 March 2001 (2001-03-21) example 1 ----- -/-	1-24															
☒ 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		Date of mailing of the international search report															
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/038079

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