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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 September 2015 (03.09.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/131027 A1

(51) International Patent Classification:
C09D 11/322 (2014.01) *C09D 11/30* (2014.01)

(21) International Application Number:
PCT/US2015/017952

(22) International Filing Date:
27 February 2015 (27.02.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/945,956 28 February 2014 (28.02.2014) US
61/977,787 10 April 2014 (10.04.2014) US

(71) Applicant: **SUN CHEMICAL CORPORAITON** [US/US]; 35 Waterview Boulevard, Parsippany, NJ 07054 (US).

(72) Inventor; and
(71) Applicant *(for US only)*: **HERLIHY, Shaun** [GB/GB]; 6 Fagus Close, Walderslade, Chatham ME5 9DD (GB).

(74) Agents: **ACHKAR, Charles, C.** et al.; Ostrolenk Faber LLP, 1180 Avenue of the Americas, New York, NY 10036 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2015/131027 A1

(54) Title: DIGITAL PRINTING INKS

(57) Abstract: The present invention provides digital printing inks comprising one or more acrylamides. Particularly preferred are inks containing diacetone acrylamide. The inks of the invention show good cure speed, blocking resistance, tack free cure, stability and resistance to blocking, and adhesion to the substrate. The inks of the invention are useful for replacing the currently used inks containing odiferous and toxic components.

DIGITAL PRINTING INKS

[001] This application claims priority to Provisional Application Nos. 61/945,956, filed February 28, 2014, and 61/977,787, filed April 10, 2014, both of which are hereby incorporated herein in their entirety.

FIELD OF THE INVENTION

[002] The present invention is directed to inks that have good cure speed, blocking resistance, tack free cure, stability, and adhesion to the substrate. The inks of the invention are useful for replacing the currently used inks containing odiferous and toxic components.

BACKGROUND

[003] Digital printing inks, particularly inkjet and aerosol jet inks, can be applied to a variety of substrates to fulfill different market needs. In some markets, such as graphics for banners and side panels of vehicles, the inks are required to be very flexible, or cracking can result when the substrate is deformed. Traditional UV inkjet inks based on multifunctional monomers meet the technical needs of fast cure and good resistance properties, but are far too low in their flexibility and generally have poor adhesion properties to plastics, and so easily result in cracking and ink removal.

[004] The use of very flexible inks based on monofunctional monomers is fundamentally unsatisfactory because of the very slow cure speeds, and the very low hardness and resistance properties that result. The biggest limitation is that the resultant inks are typically very tacky immediately after cure, and very prone to marking or set-off in a stack or roll. There is also a movement towards faster cure speed as inkjet heads develop greater capability, and as there are moves toward lower energy light sources such as light emitting diodes (LEDs) or lower power consumption medium pressure mercury lamps. This puts more pressure on the inkjet inks to be fast curing and tack free at low energy levels.

[005] Many digital printing ink manufacturers have overcome these limitations of monofunctional only inks by combining the monofunctional monomer with a material such as N-vinyl caprolactam (NVC) or N-vinyl pyrrolidone (NVP) (*see, for example,* EP2399965 and US2012/0026235). These materials have the particular advantage of eliminating the surface tack and have become an essential part of modern formulating. However, NVP has been the

subject of severe use restrictions in Europe for a number of years as a result of its adverse toxicology, and in particular the fact that it is suspected of causing cancer. The use of N-vinylcaprolactam in printing inks within Europe will now also be restricted based on a recently revised toxicity classification, with this material already not well liked within the marketplace because of the high odor that occurs on cure that is particularly apparent in the print room.

[006] What is also known by those skilled in the art is that the advantageous adhesion benefits of using an ink based on monofunctional monomers in combination with N-vinyl materials such as NVP and NVC is quickly compromised by incorporation of multifunctional monomers, with the compromise to adhesion generally being greater with higher functionality monomers. Typically an ink based on monofunctional monomers and NVP or NVC would start to lose its broad spectrum adhesion profile at levels of difunctional monomer greater than 10 wt%, or levels of trifunctional and higher acrylate monomers greater than 5 wt%

[007] In order to fulfill market requirements for digital printing inks it is also preferable to provide inks which either eliminate or contain small amounts of materials which are high odor and particularly offensive to the olfactory system, or materials which carry labeling classifications that would adversely affect the product labeling and perception of toxicity of inks in use. Examples of such monomers, which are known to have particularly high and unpleasant odor, and which should preferably be limited in any such digital printing ink formulations include: benzyl acrylate, 2-propyl heptyl acrylate, 2-carboxyethoxy acrylate, 2-methoxy ethyl acrylate, tetrahydrofurfuryl acrylate and monomers with cyclopentadienyl based structures such as dicyclopentyl acrylate, dicyclopentenyloxyethyl acrylate, dicyclopentanyl acrylate and dihydrocyclopentadienyl acrylate.

[008] Other monomers which are known to have some adverse effect on odor, but which are not immediately unpleasant and can preferably be used at relatively low levels as part of a printing ink include, for example isobornyl acrylate, *t*-butyl cyclohexyl acrylate and 3,3,5-trimethyl cyclohexyl acrylate.

[009] The EU regulation 1272/2008 ANNEX VI and subsequent amendments ("classification, labeling and packaging of substances mixtures"), commonly known as CLP, defines the toxicity categories for commercial chemicals within the EU. In addition, data is also available from individual suppliers according to the Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) registration requirements. Particularly problematic labeling for the perception of a printing ink in use would be the classifications concerned with skin, eye or respiratory system damage because of the potential to cause harm to a printer or other worker handling such materials. The most relevant and problematic labeling classifications in this regard, and acrylate monomers which trigger these labels, are listed below, and would typically trigger the ink to be labeled with a "corrosive" or "exploding chest" pictogram; H314, causes severe skin burns and eye damage (for example 2-ethoxyethoxyethylacrylate), H318, causes severe eye damage/irritation (for example 2-ethoxyethoxyethylacrylate, dipropylene glycol diacrylate, polyethylene glycol diacrylate and N-acryloyl morpholine (ACMO)) and H372 causes damage to organs through prolonged or repeated exposure (for example N-vinyl caprolactam)

[0010] The use of N-vinylcaprolactam is now particularly troublesome because despite its unique formulating properties, it's use in printing inks in Europe will be restricted based on a revised toxicity classification of H372, causes damage to organs through prolonged or repeated exposure, H319, causes serious eye irritation, H317, may cause allergenic skin reaction and H302, harmful if swallowed. It is well-known by those skilled in the art in the field of UV inkjet inks that the tertiary acrylamide UV monomer ACMO is a useful technical alternative (WO 2006041004), but even this is undesirable because of its severe eye irritancy and damage to organs through prolonged or repeated exposure classifications. Several other acrylamides are available commercially, such as those sold by KOHJIN Film and Chemicals Ltd, or MRC Unitec, but these too typically have toxicological concerns and should preferably be limited or avoided in ink-jet formulations. For example:

N,N-dimethyl acrylamide (H311, toxic in contact with the skin, H331, toxic if inhaled),

N-hydroxyethyl acrylamide (H318 causes serious eye damage, H373 may cause damage to organs through prolonged or repeated exposure),

N-isobutoxymethyl acrylamide (H311 toxic in contact with skin, H340 may cause genetic defects, H350 may cause cancer, H360 may damage fertility or the unborn child),
N-(hydroxymethyl) acrylamide (H301 toxic if swallowed, H317 may cause allergenic skin reaction, H372 causes damage to organs through prolonged or repeated exposure, H350 may cause cancer, H340 may cause genetic defects, H361 suspected of damaging fertility or the unborn child)

[0011] What is clear is that there is currently no suitable approach to producing fast curing inkjet inks which do not contain N-vinyl compounds such as NVP and NVC or other substances of toxicological concern, and yet still have good adhesion and particularly low surface tack, which would prevent them from blocking in a stack or to the reverse of the next layer within a roll.

[0012] WO 2006/041004 describes a UV curable printing ink comprising an acrylamide monomer with a trifunctional or higher acrylate monomer. The trifunctional or higher acrylate monomer is present in high amounts. Inclusion of large amounts of a trifunctional or higher monomer would, as known by those skilled in the art, compromise the adhesion properties of the printing ink.

[0013] EP 2644664 provides an actinic radiation curable composition for use in an in-mold molded article. The composition includes at a minimum an oligomer, an acrylamide derivative, and an N-vinyl compound. The document describes only N-vinyl lactams, and most preferably N-vinylcaprolactam (NVC). NVC has a relatively high odor on cure and a poor toxicological profile. The examples include formulations that contain high levels of N-vinyl caprolactam and 2-ethoxyethoxyethyl acrylate (EOEOEA), which carry adverse product labeling, and high levels of the monomer dicyclopentanyl methacrylate (Fancryl FA-513M), which has a very unpleasant odor.

[0014] EP 2302007 describes ink compositions that include photoinitiators containing a 4-thiophenyl substituted benzophenone group within the structure. Compounds of the examples contain high levels of NVC, EOEOEA, tetrahydrofurfuryl acrylate (THFA), or

dicyclopentenyloxyethyl acrylate (Fancryl FA-512A), all of which have an extremely unpleasant odor and/or carry adverse toxicological labeling.

[0015] EP 2505622 describes water-based UV curing ink jet inks comprising acrylamides. There is no disclosure of the potential use of acrylate monomers as part of the formulation.

[0016] US 7,297,460 describes inkjet inks that contain polyhedral oligomeric silesquioxane (POSS), optionally substituted with secondary acrylamide or methacrylamide functional groups. All acrylamide compounds described are acrylamide functional POSS.

[0017] WO 2010/150023 discloses a UV ink that is curable by exposing the ink to UV radiation from an LED source, followed by UV radiation from a flash lamp. The application describes a UV ink that contains an N-vinylamide or an acrylamide (N-acryloyl amines), and defines ACMO as preferred. However, the working examples contain only NVC as an amide compound of this type. In addition, all the examples and claims deem that the inclusion of multifunctional monomers is desirable.

[0018] WO 2008/093071 discloses the use of a cyclic monofunctional acrylate monomer and an acyclic hydrocarbon monomer in inkjet ink. Reference is made to the use of N-vinyl amides and acrylamides. However, all the practical examples are based on NVC.

[0019] WO 2008/117,092 discloses use of an inkjet formulation that is resistant to blocking on a reel, and makes reference to the use of N-vinyl amides and acrylamides, and multifunctional acrylate monomers. All the examples are based on NVC. As discussed above, NVC has an unpleasant odor and adverse toxicological profile.

[0020] Thus, a need exists to develop an inkjet ink that has the desired properties, but does not contain, or contains a very small amount of, components with unpleasant odor and/or adverse toxicological profiles that are currently used.

SUMMARY OF THE INVENTION

[0021] In contrast to the problems of using N-vinylcaprolactam, the subject of the present invention includes the use of acrylamides, and in particular diacetone acrylamide, which is both low odor in comparison to N-vinylcaprolactam, and carries much more favorable labeling classifications.

[0022] What we have found, which is surprising and nonobvious, is that the use of the secondary acrylamide monomer diacetone acrylamide leads to an ink which has very low surface tack, high cure speed and good blocking resistance whilst also retaining relatively low odor on cure. This is particularly surprising based on the poorer performance of other similar monomers, such as N-isopropyl acrylamide (as claimed as the preferred material in EP 2644664) since diacetone acrylamide does not possess additional functional groups that would be recognized by those skilled in the art to be involved in the polymerization process. Other key properties of the cured inks such as adhesion and flexibility are also maintained using this invention.

[0023] In a certain aspect, the present invention provides a digital printing ink comprising:

a) 1-60 wt% of an acrylamide material or blends thereof;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0024] In a certain aspect, the present invention provides a digital printing ink comprising:

a) 1-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;

d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0025] In a certain aspect, the present invention provides a water-based digital printing ink comprising:

a) 0.5-60 wt% of an acrylamide material or blends thereof;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0026] In a certain aspect, the present invention provides a water-based digital printing ink comprising:

a) 0.5-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;

h) 0-5 wt% of N-vinyl compounds;

i) 1-80 wt% water; and

j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0027] In certain embodiments, the acrylamide material is selected from the group consisting of diacetone acrylamide, N-isobutoxymethyl acrylamide, N-isopropyl acrylamide, N,N'-methylene bisacrylamide, or 2-(prop-2-enamido)ethylacetate, or a combination thereof

[0028] In another embodiment, the majority of the acrylamide material is diacetone acrylamide.

[0029] In another embodiment, all of the acrylamide material comprises diacetone acrylamide.

[0030] In certain embodiments, the monofunctional acrylate monomer, or blends thereof, comprises no more than 25 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

[0031] In certain embodiments, the monofunctional monomer, or blends thereof, comprises 0.1-20 wt% of isobornyl acrylate, t-butyl cyclohexyl acrylate and 3,3,5-trimethyl cyclohexyl acrylate.

[0032] In certain embodiments, the monofunctional monomer, or blends thereof, comprises 0.1-10 wt% of isobornyl acrylate, t-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

[0033] In certain embodiments, the monofunctional monomer, or blends thereof, comprises 0.1-5 wt% of isobornyl acrylate, t-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

[0034] In certain embodiments, the monofunctional monomer, or blends thereof, contains no isobornyl acrylate, t-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

[0035] In certain embodiments, the ink contains no N-vinyl compounds.

[0036] In certain embodiments, the ink contains no difunctional or higher monomers.

[0037] In one embodiment, the photoinitiator is present in an amount of 0.1-20 wt%.

[0038] In one embodiment, the water is present in an amount of 20-80 wt%.

[0039] In another embodiment, the water is present in an amount of 60-70 wt%.

[0040] In another embodiment, the water is present in an amount of 30-70 wt%.

[0041] In another embodiment, the water is present in an amount of 40-50 wt%.

[0042] In another embodiment, the water is present in an amount of 20-30 wt%.

[0043] In one embodiment, the solvent is present in an amount of 1-30 wt%.

[0044] In another embodiment, the solvent is present in an amount of 1-20 wt%.

[0045] In certain embodiments, the acrylated polyurethane dispersion is present in an amount of 20-30 wt%.

[0046] In one embodiment, the acrylamide material is present in an amount of 0.5-40 wt% of the ink.

[0047] In another embodiment, the acrylamide material is present in an amount of 0.5-30 wt% of the ink.

[0048] In another embodiment, the acrylamide material is present in an amount of 0.5-20 wt% of the ink.

[0049] In another embodiment, the acrylamide material is present in an amount of 0.5-10 wt% of the ink.

[0050] In another embodiment, the acrylamide material is present in an amount of 0.5-5 wt% of the ink.

[0051] In one embodiment, the ink further comprises a colorant.

[0052] In one embodiment, the ink further comprises one or more additives selected from the group consisting of stabilizers, surfactants, defoamers, slip additives, wetting additives and synergists.

[0053] In one embodiment, the ink is an ink jet ink.

[0054] In another embodiment, the ink is an aerosol jet ink.

[0055] In a particular aspect, the present invention provides a method of making a digital ink, comprising mixing:

a) 1-60 wt% of an acrylamide material or blends thereof;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0056] In a particular aspect, the present invention provides a method of making a digital ink, comprising mixing:

a) 1-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0057] In a particular aspect, the present invention provides a method of making a water-based digital printing ink, comprising mixing:

a) 0.5-60 wt% of an acrylamide material or blends thereof;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0058] In a particular aspect, the present invention provides a method of making a water-based digital printing ink, comprising mixing:

a) 0.5-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;

b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0059] In one aspect, the present invention provides a use of the digital printing ink, comprising printing the ink onto a substrate.

[0060] In one aspect, the present invention provides a printed article comprising the digital ink.

BRIEF DESCRIPTION OF THE DRAWINGS

[0061] Figure 1: Shows the effect of increasing concentrations of diacetone acrylamide (0-30%) on the effective radiation cure dose for inks 2A-2E.

[0062] Figure 2: Shows the effect of increasing concentrations of N-isopropyl acrylamide (0-20%) on the effective radiation cure dose for inks 3A-3D.

[0063] Figure 3: Shows the effect of increasing concentrations of N-isobutoxymethyl acrylamide (0-30%) on the effective cure dose for inks 4A-4E.

DETAILED DESCRIPTION OF THE INVENTION

[0064] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only, and are not restrictive of any subject matter claimed.

[0065] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which the inventions belong. All patents, patent applications, published applications and publications, websites and other published materials referred to throughout the entire disclosure herein, unless noted otherwise, are incorporated by reference in their entirety for any purpose.

[0066] In this application, the use of the singular includes the plural unless specifically stated otherwise. As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0067] In this application, the use of "or" means "and/or" unless stated otherwise.

[0068] As used herein, the terms "comprises" and/or "comprising" specify the presence of the stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. Furthermore, to the extent that the terms "includes," "having," "has," "with," "composed," "comprised" or variants thereof are used in either the detailed description or the claims, such terms are intended to be inclusive in a manner similar to the term "comprising."

[0069] As used herein, ranges and amounts can be expressed as "about" a particular value or range. "About" is intended to also include the exact amount. Hence "about 5 percent" means "about 5 percent" and also "5 percent." "About" means within typical experimental error for the application or purpose intended.

[0070] As used herein, the term "monofunctional acrylate monomer" refers to a monomer containing one functional acrylate group.

[0071] As used herein, the term "multifunctional acrylate monomer" refers to a monomer having two or more functional acrylate groups.

[0072] As used herein, the term "difunctional acrylate monomer" refers to a monomer containing two functional acrylate groups.

[0073] As used herein, the term "trifunctional acrylate monomer" refers to a monomer containing three functional acrylate groups.

[0074] As used herein, the term "or higher" when referring to an acrylate monomer means a monomer containing greater than three functional acrylate groups.

[0075] As used herein, the terms "(meth)acrylate" and "(meth)acrylic acid" include both the acrylate and methacrylate compounds.

[0076] As used herein, the term "ethoxylated" refers to chain extended compounds through the use of ethylene oxide.

[0077] As used herein, the term "propoxylated" refers to chain extended compounds through the use of propolyene oxide.

[0078] As used herein, the term "alkoxylated" refers to chain extended compounds using either or both ethylene oxide and propylene oxide.

[0079] Throughout this disclosure, all parts and percentages are by weight (wt% or mass% based on the total weight) and all temperatures are in °C unless otherwise indicated.

[0080] In a certain aspect, the present invention provides a digital printing ink comprising:

a) 1-60 wt% of an acrylamide material or blends thereof;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0081] In a certain aspect, the present invention provides a digital printing ink comprising:

a) 1-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0082] In a certain aspect, the present invention provides a water-based digital printing ink comprising:

a) 0.5-60 wt% of an acrylamide material or blends thereof;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0083] In a certain aspect, the present invention provides a water-based digital printing ink comprising:

a) 0.5-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;

b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0084] In a particular aspect, the present invention provides a method of making a digital ink, comprising mixing:

a) 1-60 wt% of an acrylamide material or blends thereof;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0085] In a certain aspect, the present invention provides a method of making a digital ink, comprising mixing:

a) 1-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;

f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0086] In a particular aspect, the present invention provides a method of making a water-based digital printing ink, comprising mixing:

a) 0.5-60 wt% of an acrylamide material or blends thereof;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0087] In a particular aspect, the present invention provides a method of making a water-based digital printing ink, comprising mixing:

a) 0.5-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and

j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

[0088] It is the intention of the present invention to provide energy curable inks, especially digital inks, which comprise an acrylamide, or combination of acrylamides. In a preferred embodiment, the acrylamide would be diacetone acrylamide either alone, or in combination with other acrylamides. More preferred would be an ink where the diacetone acrylamide is either the only acrylamide material present in the ink or is the majority of the acrylamide present in the ink.

[0089] It is a further intention of the present invention to provide energy curable inks, especially digital inks, which are based on monofunctional monomers. If difunctional monomers are used, they would preferably be used at 10 wt% or less, more preferably at 5 wt% or less. If trifunctional (or higher) monomers are used, they would preferably be used at 5 wt% or less, more preferably at 2.5 wt% or less.

[0090] It is a further intention of the present invention to provide energy curable inks, especially digital inks, which are preferably free of any N-vinyl compounds (especially N-vinyl caprolactam (NVC) and N-vinyl pyrrolidone (NVP)). If N-vinyl compounds are present, they would preferably be used at 10 wt% or less, more preferably at 5 wt% or less, even more preferably at 2 wt% or less, and most preferably eliminated altogether from the formulations.

[0091] The monomer diacetone acrylamide provides very fast curing, particularly with reference to "surface tack". Somewhat surprisingly, compared to other similar low molecular weight acrylamides, it also cures at lower doses despite an absence of any other recognized polymerizable groups within the structure. These properties make it a technically suitable alternative to the widely used N-vinyl caprolactam.

[0092] The hazard classification of the commercial monomer N-vinyl caprolactam has recently changed and, by agreement with the European Printing Ink Association (EuPIA), ink

suppliers are obliged to remove this material from their formulations. NVC is generally regarded as a unique monomer with no viable alternatives.

[0093] The use of diacetone acrylamide as part of a preferably monofunctional ink formulation gives fast, tack-free curing. Unlike many acrylamide compounds, it also has a very favorable toxicology profile and a low hazard classification based on toxicology data from its widespread commercial use in water-based emulsion polymer formulations.

[0094] The present invention is drawn to digital printing inks comprising one or more acrylamides, preferably diacetone acrylamide either alone or in combination with other acrylamides, that are very effective in providing fast curing and an unusually hard tack-free surface, which makes the inks far more resistant to blocking/setting off in a stack or reel. The inks also have excellent adhesion properties.

[0095] The energy curable inks covered by the present invention preferably show a reduced tendency to block (*i.e.* to transfer color in a stack or reel) by virtue of being very hard and fast curing. Preferably, this does not come at the expense of either the flexibility or the adhesion. The inks preferably contain 1-40%, more preferably 1-30% of one or more acrylamide materials, preferably comprising diacetone acrylamide either alone or in combination with other acrylamides, along with other monofunctional or multifunctional acrylate monomers dependent on the balance of properties being sought, but would preferably be of a low odor nature.

[0096] Preferably, the inks of the present invention would contain less than 20% of materials which are high odor and particularly offensive to the olfactory system, or materials which carry labeling classifications that would adversely affect the product labeling and perception of toxicity of inks in use, more preferably less than 10%, even more preferably less than 5%, and most preferably less than 1%. Examples of such monomers, which are known to have particularly high and unpleasant odor, and which should preferably be limited in any such digital printing ink formulations include; benzyl acrylate, 2-propyl heptyl acrylate, 2-carboxyethoxy acrylate, 2-methoxy ethyl acrylate, tetrahydrofurfuryl acrylate and monomers with cyclopentadienyl based structures such as dicyclopentyl acrylate,

dicyclopentenyloxyethyl acrylate, dicyclopentanyl acrylate and dihydrocyclopentadienyl acrylate.

[0097] Other monomers which are known to have some adverse effect on odor, but which are not immediately unpleasant and can preferably be used at relatively low levels as part of a printing ink include, for example, isobornyl acrylate, *t*-butyl cyclohexyl acrylate and 3,3,5-trimethyl cyclohexyl acrylate. These materials would preferably be used at less than 20 wt%, more preferably at less than 15 wt%

[0098] It is understood that the inks of the present formulation could contain virtually any raw materials that are compatible with energy curable and water-based ink systems. A partial list of some of the classes of materials that could be used to formulate the inks of the present invention is included below.

[0099] The ink composition according to the present invention may include water. This would preferably not contain ionic impurities, and is therefore preferably ion exchanged or distilled water. Particularly for water-based compositions, the quantity of water used according to the present invention, including that which is supplied as part of raw materials used, is preferably 20 to 80 wt%, more preferably 30 to 70 wt% by mass according to the entire ink composition.

[00100] The ink may also contain one or more water-compatible organic solvents, preferably at a level of between 1 and 30 wt%, more preferably 1 to 20 wt% by mass according to the entire ink composition, which have a primary function as a humectant, preventing drying of the ink in the inkjet heads and thus preventing them from clogging, and a secondary function as a wetting aid, allowing the inkjet drops to spread on the substrate. Examples of suitable solvents would include materials which are not highly flammable or volatile, typically an alkylene glycol ether or ether acetate type, with the following non-limiting examples: 4-hydroxy-4-methyl-2-pentanone, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol monoethyl ether acetate, diethylene glycol monopropyl ether, dipropylene glycol ethyl ether, dipropylene glycol methyl ether, ethylene glycol butyl ether, ethylene glycol ethyl ether, ethylene glycol isopropyl ether, ethylene

glycol methyl ether, ethylene glycol propyl ether, glycerine carbonate, N-methyl 2-pyrrolidone, propylene glycol, propylene glycol ethyl ether, propylene glycol ethyl ether acetate, propylene glycol methyl ether, propylene glycol n-propyl ether, triethylene glycol butyl ether, triethylene glycol methyl ether, tripropylene glycol and tripropylene glycol methyl ether.

[00101] Examples of suitable monofunctional ethylenically unsaturated monomers include, but are not limited, to the following: isobutyl acrylate; cyclohexyl acrylate; iso-octyl acrylate; n-octyl acrylate; isodecyl acrylate; iso-nonyl acrylate; octyl/decyl acrylate; lauryl acrylate; 2- propyl heptyl acrylate; tridecyl acrylate; hexadecyl acrylate; stearyl acrylate; iso-stearyl acrylate; behenyl acrylate; tetrahydrofurfuryl acrylate; 4-t.butyl cyclohexyl acrylate; 3,3,5-trimethylcyclohexane acrylate; isobornyl acrylate; dicyclopentyl acrylate; dihydrodicyclopentadienyl acrylate; dicyclopentenyloxyethyl acrylate; dicyclopentanyl acrylate; benzyl acrylate; phenoxyethyl acrylate; 2-hydroxy-3-phenoxypropyl acrylate; alkoxylated nonylphenol acrylate; cumyl phenoxyethyl acrylate; cyclic trimethylolpropane formal acrylate; 2(2-ethoxyethoxy) ethyl acrylate; polyethylene glycol monoacrylate; polypropylene glycol monoacrylate; caprolactone acrylate; ethoxylated methoxy polyethylene glycol acrylate; methoxy triethylene glycol acrylate; tripropyleneglycol monomethyl ether acrylate; diethyleneglycol butyl ether acrylate; alkoxylated tetrahydrofurfuryl acrylate; ethoxylated ethyl hexyl acrylate; alkoxylated phenol acrylate; ethoxylated phenol acrylate; ethoxylated nonyl phenol acrylate; propoxylated nonyl phenol acylate; polyethylene glycol o-phenyl phenyl ether acrylate; ethoxylated p-cumyl phenol acrylate; ethoxylated nonyl phenol acrylate; alkoxylated lauryl acrylate; ethoxylated tristyrylphenol acrylate; N-(acryloyloxyethyl)hexahydrophthalimide; N-butyl 1,2 (acryloyloxy) ethyl carbamate; acryloyl oxyethyl hydrogen succinate; octoxypolyethylene glycol acrylate; octafluoropentyl acrylate; 2-isocyanato ethyl acrylate; acetoacetoxy ethyl acrylate; 2-methoxyethyl acrylate; dimethyl aminoethyl acrylate; 2-carboxyethyl acrylate; 4-hydroxy butyl acrylate; combinations thereof, and the like. As used herein, the term ethoxylated refers to chain extended compounds through the use of ethylene oxide, propoxylated refers to chain extended compounds through the use of propylene oxide, and alkoxylated refers to chain extended compounds using either or both ethylene oxide and propylene oxide. Equivalent methacrylate compounds are also capable of being used,

although those skilled in the art will appreciate that methacrylate compounds have lower reactivity than their equivalent acrylate counterparts:

[00102] Examples of suitable multifunctional ethylenically unsaturated monomers include but are not limited to the following: 1,3-butylene glycol diacrylate; 1,4-butanediol diacrylate; neopentyl glycol diacrylate; ethoxylated neopentyl glycol diacrylate; propoxylated neopentyl glycol diacrylate; 2-methyl-1,3-propanediyl ethoxy acrylate; 2-methyl-1,3-propanediol diacrylate; ethoxylated 2-methyl-1,3-propanediol diacrylate; 3 methyl 1,5- pentanediol diacrylate; 2-butyl-2-ethyl-1,3-propanediol diacrylate; 1,6-hexanediol diacrylate; alkoxylated hexanediol diacrylate; ethoxylated hexanediol diacrylate; propoxylated hexanediol diacrylate; 1,9-nonanediol diacrylate; 1,10 decanediol diacrylate; ethoxylated hexanediol diacrylate; alkoxylated hexanediol diacrylate; diethyleneglycol diacrylate; triethylene glycol diacrylate; tetraethylene glycol diacrylate; polyethylene glycol diacrylate; propoxylated ethylene glycol diacrylate; dipropylene glycol diacrylate; tripropyleneglycol diacrylate; polypropylene glycol diacrylate; poly (tetramethylene glycol) diacrylate; cyclohexane dimethanol diacrylate; ethoxylated cyclohexane dimethanol diacrylate; alkoxylated cyclohexane dimethanol diacrylate; polybutadiene diacrylate; hydroxypivalyl hydroxypivalate diacrylate; tricyclodecanedimethanol diacrylate; 1,4-butanediylbis[oxy(2-hydroxy-3,1-propanediyl)]diacrylate; ethoxylated bisphenol A diacrylate; propoxylated bisphenol A diacrylate; propoxylated ethoxylated bisphenol A diacrylate; ethoxylated bisphenol F diacrylate; 2-(2-vinyloxyethoxy)ethyl acrylate; dioxane glycol diacrylate; ethoxylated glycerol triacrylate; glycerol propoxylate triacrylate; pentaerythritol triacrylate; trimethylolpropane triacrylate; caprolactone modified trimethylol propane triacrylate; ethoxylated trimethylolpropane triacrylate; propoxylated trimethylol propane triacrylate; tris (2-hydroxy ethyl) isocyanurate triacrylate; e-caprolactone modified tris (2-hydroxy ethyl) isocyanurate triacrylate; melamine acrylate oligomer; pentaerythritol tetraacrylate; ethoxylated pentaerythritol tetraacrylate; di-trimethylolpropane tetra acrylate; dipentaerythritol pentaacrylate; dipentaerythritol hexaaacrylate; ethoxylated dipentaerythritol hexaacrylate; combinations thereof, and the like. The term ethoxylated refers to chain extended compounds through the use of ethylene oxide, propoxylated refers to chain extended compounds through the use of propylene oxide, and alkoxylated refers to chain extended compounds using either or both ethylene oxide and propylene oxide. Equivalent methacrylate compounds are also capable of being used, although those skilled in the art will

appreciate that methacrylate compounds have lower reactivity than their equivalent acrylate counterparts.

[00103] Other functional monomer classes capable of being used in part in these formulations include cyclic lactam such as N-vinyl caprolactam; N-vinyl oxazolidinone and N-vinyl pyrrolidone, and secondary or tertiary acrylamides such as N-acryloyl morpholine; diacetone acrylamide; N-methyl acrylamide; N-ethyl acrylamide; N-isopropyl acrylamide; N-*t*-butyl acrylamide; N-hexyl acrylamide; N-cyclohexyl acrylamide; N-octyl acrylamide; N- *t*-octyl acrylamide; N-dodecyl acrylamide; N-benzyl acrylamide; N-(hydroxymethyl)acrylamide; N-isobutoxymethyl acrylamide; N- butoxymethyl acrylamide; N,N-dimethyl acrylamide; N,N-diethyl acrylamide; N,N-propyl acrylamide; N,N-dibutyl acrylamide; N,N-dihexyl acrylamide; N,N-dimethylamino methyl acrylamide; N,N-dimethylamino ethyl acrylamide; N,N-dimethylamino propyl acrylamide; N,N-dimethylamino hexyl acrylamide; N,N-diethylamino methyl acrylamide; N,N-diethylamino ethyl acrylamide; N,N-diethylamino propyl acrylamide; N,N-dimethylamino hexyl acrylamide; and N,N'-methylenebisacrylamide.

[00104] Suitable acrylated polyurethane dispersions include MS 10/1312 and MS 10/1311 from Allnex; Neorad R-440, R-441, R-444, R-447, R-448, R-465, UV-14, UV-20, UV-65, UV-TN6711 (DSM), Laromer LR8949, LR8983, LR9005, UA9059, UA9060, UA9064, and UA9095 from BASF; and Bayhydrol UV 2282, UV 2317, UV VP LS 2280, UV VP LS 2317, UV XP 2629, UV XP 2687, UV XP 2689, UV XP 2690, and UV XP 2775 from Bayer.

[00105] Suitable acrylate and non-functional resin technologies include acrylated polyester dispersions such as the Laromer PE range from BASF; water soluble epoxy acrylates such as Laromer 8765 from BASF and CN132 from Sartomer; styrene maleic anhydride adducts (SMA) where the anhydride group of a styrene-maleic copolymer is reacted with a OH-functional monomer; acetoacetate-functional polymers such as acetoacetate-functional poly(vinyl alcohol) Gohsenx Z from Nippon Gohsei; acrylic emulsions such as those sold under the trade names Joncryl (BASF), Revacryl (Synthomer), Hycar (Lubrizol), Neocryl (DSM), Neboplast (Necarbo), and the Picassian AC range (Picassian Polymers); solution acrylics such as those sold under the trade names Joncryl (BASF), poly(meth)acrylic acid such as those sold under the trade name Sokalan (BASF); polyurethane dispersions such as

those sold under the trade names Sancure (Lubrizol), Syntegra (Dow), Luplen (BASF), and Beetafin (BIP); polyester emulsions such as those sold under the trade names Eastek (Eastman), PVC Emulsions such as those sold under the trade names Vycar (Lubrizol); polyamide dispersions such as those sold under the trade names Casamid (Thomas Swann) and Hydrosize (Michelman); waterbased alkyds such as those sold under the trade names Synaqua (Arkema); poly(vinyl alcohol) such as those sold by Kuraray, Nippon Gohsei & Celanese; polyethylene glycols; poly(vinyl) pyrrolidones such as those sold under the trade names PVP-K15, K30, K60, K90 (ISP); maleic resins such as those sold under the trade names Hydrorez (Lawter); and natural resins such as waterbased shellacs (Worlee), Procote (DOW), and Revertex (Synthomer). These various resin types may, where applicable, be neutralized using organic bases including but not limited to ammonia, triethanolamine, triisopropanolamine, dimethyl aminoethanol or arginine. Alternatively, they may be neutralised by an inorganic base including, but not limited to, alkali metal oxides, alkali metal hydroxides or alkali metal carbonates, with sodium hydroxide or potassium hydroxide being the preferred inorganic bases.

[00106] Suitable photoinitiators include, but are not limited to, the following: α-hydroxyketones, including, but not limited to, 1-hydroxy-cyclohexyl-phenyl-ketone, 2-hydroxy-2-methyl-1-phenyl-1-propanone; 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl}-2-methyl-propan-1-one; and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone; acylphosphine oxides including, but not limited to 2,4,6-trimethylbenzoyl-diphenylphosphine oxide; 2,4,6-trimethylbenzoyl-diphenyl phosphinate; and bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide; and α-aminoketones including, but not limited to, 2-methyl-1-[4-methylthio)phenyl]-2-morpholinopropan-1-one; 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan -1-one; and 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one; combinations thereof, and the like.

[00107] Examples of other suitable photoinitiators include benzyl dimethyl ketal; thioxanthone initiators such as 2-4-diethylthioxanthone, isopropylthioxanthone, 2-chlorothioxanthone, and 1-chloro-4-propoxythioxanthone; benzophenone initiators such as benzophenone, 4-phenylbenzophenone, 4-methylbenzophenone, 4-hydroxy benzophenone, and 4-carboxymethoxy benzophenone; methyl-2-benzoylbenzoate; 4-benzoyl-4-

methyldiphenyl sulphide; phenylglyoxylate initiators such as phenyl glyoxylic acid methyl ester, oxy-phenyl-acetic acid 2-[2-hydroxyl-ethoxy]-ethyl ester, or oxy-phenyl-acetic acid 2-[2-oxo-2-phenyl-acetoxy-ethoxy]-ethyl ester; titanocen radical initiators such as titanium-bis(η 5-2,4-cyclopentadien-1-yl)-bis-[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]; oxime ester radical initiators such as [1-(4-phenylsulfanylbenzoyl)heptylideneamino]benzoate, or [1-[9-ethyl-6-(2-methylbenzoyl)carbazol-3-yl]-ethylideneamino]acetate; plus others including methyl benzoylformate; 1-phenyl-1,2-propanedione-2-(O-ethoxycarbonyl)oxime; 4,4,4-(hexyamethyltriamino)triphenyl methane; 2-benzyl-2-dimethylamino-4-morpholinobutyrophenone; 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one; 4,4-bis(diethylamino)benzophenone; 2-ethyl anthraquinone; and the like.

[00108] Polymeric photoinitiators are also suitable, including, for example, polymeric aminobenzoates (GENOPOL AB-1 from Rahn, Omnipol ASA from IGM or Speedcure 7040 from Lambson), polymeric benzophenone derivatives (GENOPOL BP-1 from Rahn, Omnipol BP from IGM or Speedcure 7005 from Lambson), polymeric thioxanthone derivatives (GENOPOL TX-1 from Rahn, Omnipol TX from IGM or Speedcure 7010 from Lambson), and α-hydroxyketones (polyethylene glycol mono-4-(2-hydroxy-2-methyl propiophenone) ether).

[00109] An amine synergist may also be included in the ink formulation. Suitable examples include, but are not limited to, the following: ethyl-4-(dimethylamino)benzoate; 2-ethylhexyl-4-(dimethylamino)benzoate; 2-(dimethylamino)ethylbenzoate; poly[oxy(methyl-1,2-ethanediyl)]; α-[4-(dimethylamino)-α-butoxy; butoxyethyl-4-(dimethylamino)benzoate; triethanolamine, N-methyldiethanolamine, N,N-dimethylethanolamine; plus EBECRYL 80/81/83, EBECRYL LEO 10551/10552/10553, EBECRYL 7100 and EBECRYL P116 available from Cytec; CN501, CN503, CN550, CN UVA421, CN341, CN3705, CN3715, CN3735, CN3755, CN381, CN384, CN584, and CN554 all available from Sartomer; GENOMER 5142, GENOMER 5161, and GENOMER 5275 from Rahn; PHOTOMER 4771, PHOTOMER 4779F, PHOTOMER 4967F, PHOTOMER 4968F, PHOTOMER 5006F, PHOTOMER 4775F, PHOTOMER 5960F, LAROMER LR8996, LAROMER PO 94F and LAROMER PO77F, all available from BASF; OMNIRAD CI-250 and OMNILANE A1230C from IGM Resins; and DESMOLUX VPLS 2299 from Bayer Coatings.

[00110] The ink formulation can optionally include a suitable de-aerator, which prevents the formation of air inclusions and pinholes in the cured coating. These also reduce rectified diffusion, which can cause reliability issues in the printhead. Examples include the following products available from Evonik: TEGO AIREX900, 910, 916, 920, 931, 936, 940, 944, 945, 950, 962, 980, and 986.

[00111] Defoamers can also optionally be included in the formulation, which prevent the formation of foam during manufacture of the ink, and also while jetting. These are particularly important with recirculating printheads. Examples of suitable defoamers include TEGO FOAMEX N, FOAMEX 1488, 1495, 3062, 7447, 800, 8030, 805, 8050, 810, 815N, 822, 825, 830, 831, 835, 840, 842, 843, 845, 855, 860, and 883, TEGO FOAMEX K3, TEGO FOAMEX K7/K8 and TEGO TWIN 4000, all available from Evonik. Available from Byk is BYK-066N, 088, 055, 057, 1790, and 020, BYK-A 530, and 067A, and BYK 354.

[00112] Surface control additives are often optionally used to control the surface tension of the ink, which is required to adjust the wetting on the face plate of the printhead, and also to give the desired drop spread on the substrate, or, in the case of multi pass inkjet printing, wet on dry drop spread. They can also be used to control the level of slip and scratch resistance of the coating. Examples of suitable surface control additives include but are not limited to TEGO FLOW300, 370, and 425, TEGO GLIDE 100, 110, 130, 406, 410, 411, 415, 420, 432, 435, 440, 482, A115, and B1484, TEGO GLIDE ZG 400, TEGO RAD2010, 2011, 2100, 2200N, 2250, 2300, 2500, 2600, 2650, and 2700, TEGO TWIN 4000, and 4100, TEGO WET 240, 250, 260, 265, 270, 280, 500, 505, and 510 and TEGO WET KL245, all available from Evonik. Available from Byk are BYK 333, and 337, BYK UV3500, BYK 378, 347, and 361, BYK UV3530, and 3570, CERAFLOUR 998, and 996, NANOBYK 3601, 3610, and 3650 and CERMAT 258. Available from Cytec are EBECRYL 350, and 1360, MODAFLOW 9200, and EBECRYL 341. From Sartomer, the aliphatic silicone acrylate CN9800 may be used.

[00113] The ink compositions of the present invention may optionally contain one or more colorants, including pigments and/or dyes. Examples of suitable organic or inorganic pigments include carbon black, zinc oxide, titanium dioxide, phthalocyanine, anthraquinones, perylenes, carbazoles, monoazo and disazobenzimidazoles, rhodamines, indigoids,

quinacridones, diazopyranthrones, dinitroanilines, pyrazoles, diazopyranthrones, pyrazoles, dianisidines, pyranthrones, tetracholoroisoindolines, dioxazines, monoazoacrylides and anthrapyrimidines, combinations thereof, and the like. The dyes include but are not limited to azo dyes, anthraquinone dyes, xanthene dyes, azine dyes, combinations thereof and the like.

[00114] Commercial organic pigments classified according to Color Index International may be used, including, but not limited to, those according to the following trade designations: blue pigments PB1, PB15, PB15:1, PB15:2, PB15:3, PB15:4, PB15:6, PB16, PB60; brown pigments PB5, PB23, and PB265; green pigments PG1, PG7, PG10 and PG36; yellow pigments PY3, PY14, PY16, PY17, PY24, PY65, PY73, PY74 PY83, PY95, PY97, PY108, PY109,PY110, PY113, PY128, PY129,PY138, PY139, PY150, PY151, PY154, PY156, PY175, PY180 and PY213; orange pigments PO5, PO15, PO16, PO31, PO34, PO36, PO43, PO48, PO51, PO60, PO61 and PO71; red pigments PR4, PR5, PR7, PR9, PR22, PR23, PR48, PR48:2, PR49, PR112, PR122, PR123, PR149, PR166, PR168, PR170, PR177, PR179, PR190, PR202, PR206, PR207, PR224 and PR254: violet pigments PV19, PV23, PV32, PV37 and PV42; black pigments PBk1, PBk6, PBk7, PBk8, PBk9, PBk10, PBk11, PBk12, PBk13, PBk14, PBk17, PBk18, PBk19, PBk22, PBk23, PBk24, PBk25, PBk26, PBk27, PBk28, PBk29, PBk30, PBk31, PBk32, PBk33, PBk34, PBk35, NBk1, NBk2, NBk3, NBk4, NBk6; combinations thereof, and the like.

[00115] The pigments are preferably milled to typically less than 1 micrometer, with a preferred particle size distribution of 10-500 nm, and more preferably 10-350 nm, to have better transparency and a wide color gamut. The pigment dispersion will typically contain 60-90% monomer, which can be a mono or multifunctional (meth)acrylate monomer, with added stabilizer, inhibitor, dispersant and, optionally, a pigment additive/synergist and/or a wetting additive/oligomer/resin. The pigment dispersions may also be water-based pigment dispersions. The ratio of pigment to dispersant would usually be 1:2 to 9:1 depending on the chemistry of the pigment and dispersant. Typical dispersants would include EFKA 7414, 7476, 7477, 7700, 7701, 7702, 7710, 7731 and 7732 available from BASF and SOLSPERSE 1700, 1900, 24000SC/GR, 26000, 32000, 33000, 35000, 36000, 39000, 41000 and 71000 available from Lubrizol. Examples of additive/synergists to aid dispersion stability include SOLSPERSE 5000, 12000 and 22000 from Lubrizol.

[00116] The curing of the inks of the present invention normally requires a traditional mercury vapor discharge lamp to generate UV radiation for initiating the cure of energy curable inkjet inks. Solid state UV radiation sources such as UV light emitting diodes (LEDs) can also be used as the source of UV radiation. Mercury lamps also take time to heat up and cool down and have the potential to release mercury, which is highly toxic. UV LEDs can be rapidly switched on and off, are more energy efficient and don't generate heat, so are better for use with heat sensitive substrates. This is leading to a movement towards UV LED formulations, which can be more sensitive to issues with stray light as they contain photoinitiators with spectral absorbance in the UVA region of the electromagnetic spectrum. The inks of the present invention could also be formulated to cure by other radiation sources, such as, for example, microwave, infrared, electron beam, visible light, x-ray, etc.

EXAMPLES

[00117] The following examples illustrate specific aspects of the present invention and are not intended to limit the scope thereof in any respect and should not be so construed.

Example 1 – Properties of cyan ink-jet inks containing acrylamide

[00118] Cyan inkjet inks were prepared according to the formulations in Table 1. All amounts are in wt% unless specified otherwise. Ink viscosity was recorded using a Brookfield DVII viscometer at 50°C.

Table 1

Material	Source/commercial code	Examples					
		Cyan 1A (comp)	Cyan 1B (comp)	Cyan 1C (inv)	Cyan 1D (inv)	Cyan 1E (inv)	Cyan 1F (comp)
N-vinyl caprolactam	BASF, V-CAP	24.9					
Diacetone acrylamide	Sigma-Aldrich			24.9			
N-isobutoxymethyl acrylamide	MRC-Unitec, IBMA				24.9		
N-isopropyl acrylamide	Sigma-Aldrich					24.9	
N-acryloyl morpholine	RAHN, ACMO						24.9
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	18	26.3	18	18	18	18
Isobornyl acrylate	Sartomer, SR506D	12	20.3	12	12	12	12
2-Phenoxyethylacrylate	Sartomer, SR339EU	16.25	24.55	16.25	16.25	16.25	16.25

Material	Source/commercial code	Examples					
		Cyan 1A (comp)	Cyan 1B (comp)	Cyan 1C (inv)	Cyan 1D (inv)	Cyan 1E (inv)	Cyan 1F (comp)
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6	6	6
Stabilizer package		1.12	1.12	1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal acrylate		9.73	9.73	9.73	9.73	9.73	9.73
Total		**100**	**100**	**100**	**100**	**100**	**100**
Viscosity (mPas @ 50°C)		9.15	10.0	15.7	13.5	11.8	11.0

Note: "comp" = Comparative Example; "inv" = Inventive Example

Cure speed/blocking resistance

[00119] The inks in Table 1 were printed onto PE85 white Top Trans label substrate (from Avery Dennison) using a number 2 K bar and cured at doses of 50, 70 and 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. The prints were then stacked with a piece of blank Incada Excel carton board substrate (reverse side) on top and put under a pressure of 10 tons for 5 seconds in a Specac blocking tester. The cartonboard layer was removed and the level of ink blocking determined by amount of color transferred to the blank substrate using a Spectraflash 600 Spectrophotometer measuring the DL* value through a wide aperture. Lower levels of DL* indicate faster cure speed and better blocking performance due to lower ink transfer. Results are given in Table 2.

Table 2.

Example	DL* 50mJ	DL* 70mJ	DL* 150mJ
Cyan 1A	1.87	0.08	0.44
Cyan 1B	20.68	9.72	0.45
Cyan 1C	2.61	1.81	0.16
Cyan 1D	7.22	4.05	0.87

Example	DL* 50mJ	DL* 70mJ	DL* 150mJ
Cyan 1E	17.56	11.05	0.52
Cyan 1F	3.99	1.13	0.41

[00120] The results in Table 2 demonstrate that the inventive inks have varying degrees of block resistance, all of which could be satisfactory based on customer print processing and end-use requirements. The preferred diacetone acrylamide material (Example 1C), exhibits faster cure speed than the other acrylamides tested, including the well-known and widely used tertiary acrylamide ACMO, and has similar performance to N-vinylcaprolactam. The invention therefore shows excellent utility, particularly at the low cure doses which are increasingly important in the commercial environment. Example 1B contains no acrylamide or N-vinyl caprolactam and shows very poor cure performance at low doses. The inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Tack free cure

[00121] The inks in Table 1 were printed onto PE85 white Top Trans label substrate (from Avery Dennison) using a number 2 K bar and cured at doses of 70 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. The prints were then assessed for their surface tack by finger touch, both immediately and 1 hour after cure. Results are given in Table 3.

Table 3

Example	Finger tack immediately after cure	Finger tack 1 hr. after cure
Cyan 1A	Not tacky	Not tacky
Cyan 1B	Very tacky	Very tacky
Cyan 1C	Not tacky	Not tacky
Cyan 1D	Tacky	Tacky
Cyan 1E	Tacky	Slightly tacky
Cyan 1F	Slightly tacky	Not tacky

[00122] The results in Table 3 demonstrate that the inventive inks have varying degrees of cure, all of which could be satisfactory based on customer curing processing and end-use requirements. The preferred diacetone acrylamide material (Example 1C), has similar tack-free cure performance to N-vinyl caprolactam and shows much better performance than all the other acrylamides tested, including the well-known ACMO in Example 1F. The inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Stackability / Blocking

[00123] The Example inks 1A-F in Table 1 were printed onto a flexible white vinyl substrate using a 12 micron K bar and cured at a dose of 70 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. An additional piece of blank substrate was then placed face down onto the print surface and the print sandwich placed under a 2 kg weight for 6 hours. The 2 pieces of substrate were then peeled apart and the level of adhesion and ink transfer to the blank substrate assessed. The results are shown in Table 4, using the following criteria:

FAIL – The blank substrate sticks to the printed ink; and/or makes a distinct audible "crackling" noise as the sheets are separated; and/or ink transfer occurs to the top blank piece of substrate.

PASS – There is slight or no adherence between the blank substrate and the printed ink; little or no noise on separation of the sheets; little or no ink is transferred to the top blank piece of substrate; and very little or no effort is required to separate the sheets.

Table 4

Example	Stackability / Blocking
Cyan 1A	PASS
Cyan 1B	FAIL

Example	Stackability / Blocking
Cyan 1C	PASS
Cyan 1D	FAIL
Cyan 1E	FAIL
Cyan 1F	PASS

[00124] The results in Table 4 demonstrate that the inventive inks have varying degrees of blocking, all of which could be satisfactory based on customer curing processing and end-use requirements. The preferred diacetone acrylamide material (Example 1C) shows good utility and gives acceptable performance in this stackabilily / blocking test. The inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Adhesion

[00125] The inks in Table 1 were printed onto Dibond, polycarbonate, acrylic, rigid polystyrene, rigid vinyl and flexible vinyl substrates using a 12 micron K bar and cured at a dose of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. Their adhesion to the test substrates was then tested with the well-known cross hatch adhesion test (ISO 2409) using a scalpel and ISO 2409 adhesive tape from Elcometer. Results are given in numerical categories according to the amount of ink removed from zero (perfect, no ink removed) to 5 (>35% ink removed). These results are given in Table 5.

Table 5

Example	Crosshatch adhesion test results					
	Dibond	Polycarbonate	Acrylic	Rigid Polystyrene	Rigid PVC	Flexible vinyl
Cyan 1A	0	0	2	0	0	1
Cyan 1B	5	0	0	0	0	1
Cyan 1C	1	0	0	0	1	1
Cyan 1D	1	0	0	0	1	1

Example	Crosshatch adhesion test results					
	Dibond	Polycarbonate	Acrylic	Rigid Polystyrene	Rigid PVC	Flexible vinyl
Cyan 1E	1	0	1	0	0	2
Cyan 1F	1	0	2	2	3	1

[00126] The results in Table 5 demonstrate that the inventive inks have varying degrees of adhesion, all of which could be satisfactory based on customer curing processing and end-use requirements. Further, the preferred diacetone acrylamide material (Example 1C) can be used in ink-jet formulations without any significant loss of adhesion against a typical standard commercial ink containing NVC. It should also be noted that Example 1C also has superior performance to the well-known and widely used ACMO.

Examples 2, 3, 4 – Cure enhancement of ink-jet inks containing diacetone acrylamide

[00127] Cyan inkjet inks were prepared according to the formulations in Table 6. The formulations in Table 6 were prepared for each of 3 different acrylamides:

diacetone acrylamide; giving formulations 2 A-E

N-isopropyl acrylamide; giving formulations 3 A-E*

N- isobutoxymethyl acrylamide; giving formulations 4 A-E

**Note that N-isopropyl acrylamide was not soluble at 30% in the test formulation and so was not measured at that concentration.*

Table 6

Material	Source / commercial code	Examples				
		Cyan A	Cyan B	Cyan C	Cyan D	Cyan E
Acrylamide		0	5	10	20	30
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	23.72	22.05	20.39	17.05	13.72
Isobornyl acrylate	Sartomer, SR506D	23.72	22.05	20.39	17.05	13.72
2-Phenoxyethylacrylate	Sartomer, SR339EU	23.71	22.05	20.37	17.05	13.71
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6	2.6

Material	Source / commercial code	Examples				
		Cyan A	Cyan B	Cyan C	Cyan D	Cyan E
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6	6
Stabilizer package		1.12	1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal acrylate		9.73	9.73	9.73	9.73	9.73
Total		**100**	**100**	**100**	**100**	**100**

Cure speed/blocking resistance

[00128] The inks in Table 6 were printed onto PE85 white Top Trans label substrate (from Avery Dennison) using a number 2 K bar and cured at a series of defined doses between 33-204 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. The prints were then stacked with a piece of blank Incada Excel carton board substrate (reverse side) on top and put under a pressure of 10 tons for 5 seconds in a Specac blocking tester. The cartonboard layer was removed and the level of ink blocking determined by amount of color transferred to the blank substrate using a Spectraflash 600 Spectrophotometer measuring the DL* value through a wide aperture. Lower levels of DL* indicate higher cure speed and better blocking performance due to lower ink transfer. Results are given in Figures 1-3 where it is clear that increasing levels of diacetone acrylamide (Figure 1) give rise to an incremental improvement in cure performance, as shown by decreasing DL* values. In contrast, both N-isopropyl acrylamide (Figure 2) and N-isobutoxymethyl acrylamide (Figure 3) show no such advantageous increase in cure speed with increasing concentration. The inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions.

Example 5 – Properties of yellow ink-jet inks containing acrylamide

[00129] Yellow inkjet inks were prepared according to the formulations in Table 7. All amounts are in wt% unless specified otherwise. Ink viscosity was recorded using a Brookfield DVII viscometer at 50°C.

Table 7

Material	Source / commercial code	Examples			
		Yellow 5A (comp)	Yellow 5B (comp)	Yellow 5C (inv)	Yellow 5D (inv)
N-vinyl caprolactam	BASF, V-CAP	24.9			
Diacetone acrylamide	Sigma-Aldrich			24.9	
N-isobutoxymethyl acrylamide	MRC-Unitec, IBMA				24.9
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	18	26.3	18	18
Isobornyl acrylate	Sartomer, SR506D	9	17.3	9	9
2-Phenoxyethylacrylate	Sartomer, SR339EU	17.5	25.8	17.5	17.5
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	7	7	7	7
Stabilizer package		1.2	1.2	1.2	1.2
Pigment concentrate containing 16% CI Pigment Yellow 150 in cyclic trimethylolpropane formal acrylate		10.4	10.4	10.4	10.4
Total		**100**	**100**	**100**	**100**
Viscosity (mPas @ 50°C)		9.96	11.1	17.5	15.1

Tack free cure

[00130] The inks in Table 7 were printed onto PE85 white Top Trans label substrate (from Avery Dennison) using a number 2 K bar and cured at doses of 70 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. The prints were then assessed for their surface tack by finger touch, both immediately and 1 hour after cure. Results are given in Table 8.

Table 8

Example	Finger tack immediately after cure	Finger tack 1 hour after cure
Yellow 5A	Not tacky	Not tacky
Yellow 5B	Tacky	Slightly tacky

Example	Finger tack immediately after cure	Finger tack 1 hour after cure
Yellow 5C	Slightly tacky	Not tacky
Yellow 5D	Tacky	Slightly tacky

[00131] The results in Table 8 demonstrate that the inventive inks have varying degrees of cure, all of which could be satisfactory based on customer curing processing and end-use requirements. The preferred diacetone acrylamide material (Example 5C) has similar tack-free cure performance to N-vinyl caprolactam and shows much better performance than N-isobutoxymethyl acrylamide. The inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Stackability / Blocking

[00132] The yellow inks A-D in Table 7 were printed onto a flexible white vinyl substrate using a 12 micron K bar and cured at a dose of 70 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. An additional piece of blank substrate was then placed face down onto the print surface and the print sandwich placed under a 2 kg weight for 6 hours. The two pieces of substrate were then peeled apart and the level of adhesion and ink transfer to the blank substrate assessed. The results are shown in Table 9 using the following criteria:

FAIL – The blank substrate sticks to the printed ink; and/or makes a distinct audible "crackling" noise as the sheets are separated; and/or ink transfer occurs to the top blank piece of substrate.

PASS – There is slight or no adherence between the blank substrate and the printed ink; little or no noise on separation of the sheets; little or no ink is transferred to the top blank piece of substrate; and very little or no effort is required to separate the sheets.

Table 9.

Example	Stackability / Blocking
Yellow 5A	PASS
Yellow 5B	FAIL
Yellow 5C	PASS
Yellow 5D	FAIL

[00133] The results in Table 9 demonstrate that the inventive inks have varying degrees of blocking, all of which could be satisfactory based on customer curing processing and end-use requirements. The preferred diacetone acrylamide material (Example 5C) shows good utility and gives acceptable performance in yellow inks for this stackability / blocking test. The inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Example 6 – Properties of magenta ink-jet inks containing acrylamide

[00134] Magenta inkjet inks were prepared according to the formulations in Table 10. All amounts are in wt% unless specified otherwise. Ink viscosity was recorded using a Brookfield DVII viscometer at 50°C.

Table 10.

Material	Source / commercial code	Examples			
		Magenta 6A (comp)	Magenta 6B (comp)	Magenta 6C (inv)	Magenta 6D (inv)
N-vinyl caprolactam	BASF, V-CAP	24.9			
Diacetone acrylamide	Sigma-Aldrich			24.9	
N-isobutoxymethyl acrylamide	MRC-Unitec, IBMA				24.9
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	25.2	33.5	25.2	25.2
Isobornyl acrylate	Sartomer, SR506D	12	20.3	12	12
2-Phenoxyethylacrylate	Sartomer, SR339EU	5.7	14	5.7	5.7
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9

Material	Source / commercial code	Examples			
		Magenta 6A (comp)	Magenta 6B (comp)	Magenta 6C (inv)	Magenta 6D (inv)
Photoinitiator	BASF, Irgacure 184	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	4	4	4	4
Stabilizer package		1.2	1.2	1.2	1.2
Pigment concentrate containing 21% CI Pigment Violet 19 in 2-Phenoxyethylacrylate		15	15	15	15
Total		**100**	**100**	**100**	**100**
Viscosity (mPas @ 50°C)		9.15	10.0	15.1	12.7

Tack free cure

[00135] The magenta inks in Table 10 were printed onto PE85 white Top Trans label substrate (from Avery Dennison) using a number 2 K bar and cured at doses of 70 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. The prints were then assessed for their surface tack by finger touch, both immediately and 1 hour after cure. Results are given in table 11.

Table 11

Example	Finger tack immediately after cure	Finger tack 1 hour after cure
Magenta 6A	Slightly tacky	Not tacky
Magenta 6B	Tacky	Slightly tacky
Magenta 6C	Slightly tacky	Not tacky
Magenta 6D	Tacky	Slightly tacky

[00136] The results in Table 11 demonstrate that the inventive inks have varying degrees of cure, all of which could be satisfactory based on customer curing processing and end-use requirements. The preferred diacetone acrylamide material (Example 6C) has similar tack-free cure performance to N-vinyl caprolactam and shows much better performance than N-isobutoxymethyl acrylamide. The inks of the invention performed comparably to prior art

inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Stackability / Blocking

[00137] The magenta inks A-D in Table 10 were printed onto a flexible white vinyl substrate using a 12 micron K bar and cured at a dose of 70 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. An additional piece of blank substrate was then placed face down onto the print surface and the print sandwich placed under a 2 kg weight for 6 hours. The 2 pieces of substrate were then peeled apart and the level of adhesion and ink transfer to the blank substrate assessed. The results are shown in Table 12 using the following criteria:

FAIL – The blank substrate sticks to the printed ink; and/or makes a distinct audible "crackling" noise as the sheets are separated; and/or ink transfer occurs to the top blank piece of substrate.

PASS – There is slight or no adherence between the blank substrate and the printed ink; little or no noise on separation of the sheets; little or no ink is transferred to the top blank piece of substrate; and very little or no effort is required to separate the sheets.

Table 12

Example	Stackability / Blocking
Magenta 6A	PASS
Magenta 6B	FAIL
Magenta 6C	PASS
Magenta 6D	FAIL

[00138] The results in Table 12 demonstrate that the inventive inks have varying degrees of blocking, all of which could be satisfactory based on customer curing processing and end-use requirements. The preferred diacetone acrylamide material (Example 6C) shows good utility in magenta inks and gives acceptable performance in this stackabilily / blocking test. The

inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Example 7 – Properties of black ink-jet inks containing acrylamide

[00139] Black inkjet inks were prepared according to the formulations in Table 13. All amounts are in wt% unless specified otherwise. Ink viscosity was recorded using a Brookfield DVII viscometer at 50°C.

Table 13

Material	Source / commercial code	Examples			
		Black 7A (comp)	Black 7B (comp)	Black 7C (inv)	Black 7D (inv)
N-vinyl caprolactam	BASF, V-CAP	20			
Diacetone acrylamide	Sigma-Aldrich			20	
N-isobutoxymethyl acrylamide	MRC-Unitec, IBMA				20
Dipentaerythritol hexaacrylate	Sartomer, SR399	1	1	1	1
2-Phenoxyethylacrylate	Sartomer, SR339EU	55.34	75.34	55.34	55.34
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 369	1	1	1	1
Photoinitiator	Lambson, DETX	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5
Stabilizer package		1.12	1.12	1.12	1.12
Pigment concentrate containing 22.5% CI Pigment Black 7 in cyclic trimethylolpropane formal acrylate		11.54	11.54	11.54	11.54
Total		**100**	**100**	**100**	**100**
Viscosity (mPas @ 50°C)		9.24	9.63	13.6	12.3

Tack free cure

[00140] The black inks in Table 13 were printed onto PE85 white Top Trans label substrate (from Avery Dennison) using an 8 microns K bar and cured at doses of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. The prints were then assessed for their surface tack by finger touch, both immediately and 1 hour after cure. Results are given in Table 14.

Table 14

Example	Finger tack immediately after cure	Finger tack 1 hour after cure
Black 7A	Not tacky	Not tacky
Black 7B	Very tacky	Tacky
Black 7C	Slightly tacky	Not tacky
Black 7D	Slightly tacky	Slight tacky

[00141] The results in Table 14 demonstrate that the inventive inks have varying degrees of cure, all of which could be satisfactory based on customer curing processing and end-use requirements. The preferred diacetone acrylamide material (Example 7C) has similar tack-free cure performance to N-vinyl caprolactam. The inks of the invention performed comparably to prior art inks, showing that satisfactory inks can be formulated, without use of the currently used odiferous and toxic components. The inventive inks can be used instead of prior art inks, with or without minor modifications to curing conditions. In fact, inks containing diacetone acrylamide performed just as well as inks containing NVC, which is currently considered the best amide compound to use, and hereto was not considered replaceable.

Stackability / Blocking

[00142] The black inks 7A-D in table 13 were printed onto a flexible white vinyl substrate using an 8 micron K bar and cured at a dose of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. An additional piece of blank substrate was then placed face down onto the print surface and the print sandwich placed under a 2 kg weight for 6 hours. The 2 pieces of substrate were then peeled apart and the level of adhesion and ink transfer to the blank substrate assessed. The results are shown in Table 15 using the following criteria:

FAIL – The blank substrate sticks to the printed ink; and/or makes a distinct audible "crackling" noise as the sheets are separated; and/or ink transfer occurs to the top blank piece of substrate.

PASS – There is slight or no adherence between the blank substrate and the printed ink; little or no noise on separation of the sheets; little or no ink is transferred to the top blank piece of substrate; and very little or no effort is required to separate the sheets.

Table 15

Example	Stackability / Blocking
Black 7A	PASS
Black 7B	PASS
Black 7C	PASS
Black 7D	PASS

[00143] The results in Table 15 demonstrate good utility and acceptable performance for all 4 black inks for this stackability / blocking test.

Example 8 – Properties of cyan ink-jet inks containing NVC and hydroxypivalyl hydroxypivalate diacrylate multifunctional monomer

[00144] Cyan inkjet inks were prepared according to the formulations in Table 16. All amounts are in wt% unless specified otherwise. Ink viscosity was recorded using a Brookfield DVII viscometer at 50°C.

Table 16

Material	Source/commercial code	Examples								
		Cyan 8A (comp)	Cyan 8B (comp)	Cyan 8C (comp)	Cyan 8D (comp)	Cyan 8E (comp)	Cyan 8F (comp)	Cyan 8G (comp)	Cyan 8H (comp)	Cyan 8I (comp)
N-vinyl caprolactam	BASF, V-CAP	24.9	24.9	24.9	24.9	24.9	24.9	24.9	24.9	24.9
hydroxypivalyl hydroxypivalate diacrylate	Miwon , Miramer M210	0	1	2	4	6	8	10	12	15
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	18	17	16	14	12	10	8	6	3
Isobornyl acrylate	Sartomer, SR506D	12	12	12	12	12	12	12	12	12
2-Phenoxyethylacrylate	Sartomer, SR339EU	16.25	16.25	16.25	16.25	16.25	16.25	16.25	16.25	16.25

Material	Source/commercial code	Examples								
		Cyan 8A (comp)	Cyan 8B (comp)	Cyan 8C (comp)	Cyan 8D (comp)	Cyan 8E (comp)	Cyan 8F (comp)	Cyan 8G (comp)	Cyan 8H (comp)	Cyan 8I (comp)
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2	2	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2	2	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6	6	6	6	6	6
Stabilizer package		1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal acrylate		9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73
Total		**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**
Viscosity (mPas @ 50°C)		9.00	8.40	9.15	9.03	8.58	9.12	9.66	9.18	9.72

Adhesion

[00145] The inks in Table 16 were printed onto Dibond, polycarbonate, and acrylic substrates using a 12 micron K bar and cured at a dose of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. Their adhesion to the test substrates was then tested with the well-known cross hatch adhesion test (ISO 2409) using a scalpel and ISO 2409 adhesive tape from Elcometer. Results are given in numerical categories according to the amount of ink removed from zero (perfect, no ink removed) to 5 (>35% ink removed). Inks where all the ink is removed and there is no adhesion at all are also recorded. These results are given in Table 17.

Table 17

Example	Crosshatch adhesion test results		
	Dibond	Polycarbonate	Acrylic
Cyan 8A	2	0	0
Cyan 8B	3	0	0
Cyan 8C	5	0	0
Cyan 8D	No adhesion	1	1
Cyan 8E	No adhesion	1	1

Example	Crosshatch adhesion test results		
	Dibond	Polycarbonate	Acrylic
Cyan 8F	No adhesion	5	2
Cyan 8G	No adhesion	No adhesion	5
Cyan 8H	No adhesion	No adhesion	No adhesion
Cyan 8I	No adhesion	No adhesion	No adhesion

[00146] The results in Table 17 demonstrate that for monofunctional style inks containing N-vinyl caprolactam, increasing levels of the difunctional monomer hydroxypivalyl hydroxypivalate diacrylate leads to worsening adhesion when incorporated at levels of between 1-10% depending on the substrate, and total adhesion loss above 10%. The adhesion loss is associated with the increased shrinkage that comes from the use of multifunctional monomers.

Example 9 – Properties of cyan ink-jet inks containing NVC and 1,6-hexanediol diacrylate multifunctional monomer

[00147] Cyan inkjet inks were prepared according to the formulations in Table 18. All amounts are in wt% unless specified otherwise. Ink viscosity was recorded using a Brookfield DVII viscometer at 50°C.

Table 18

Material	Source/commercial code	Examples			
		Cyan 9A (comp)	Cyan 9B (comp)	Cyan 9C (comp)	Cyan 9D (comp)
N-vinyl caprolactam	BASF, V-CAP	24.9	24.9	24.9	24.9
1,6-hexanediol diacrylate	Allnex, HDDA	0	1	2	4
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	18	17	16	14
Isobornyl acrylate	Sartomer, SR506D	12	12	12	12
2-Phenoxyethylacrylate	Sartomer, SR339EU	16.25	16.25	16.25	16.25
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6

Material	Source/commercial code	Examples			
		Cyan 9A (comp)	Cyan 9B (comp)	Cyan 9C (comp)	Cyan 9D (comp)
Stabilizer package		1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal acrylate		9.73	9.73	9.73	9.73
Total		**100**	**100**	**100**	**100**
Viscosity (mPas @ 50°C)		9.00	9.33	9.36	9.00

Adhesion

[00148] The inks in Table 18 were printed onto Dibond, polycarbonate, and acrylic substrates using a 12 micron K bar and cured at a dose of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. Their adhesion to the test substrates was then tested with the well-known cross hatch adhesion test (ISO 2409) using a scalpel and ISO 2409 adhesive tape from Elcometer. Results are given in numerical categories according to the amount of ink removed from zero (perfect, no ink removed) to 5 (>35% ink removed). Inks where all the ink is removed and there is no adhesion at all are also recorded. These results are given in Table 19.

Table 19

Example	Crosshatch adhesion test results		
	Dibond	Polycarbonate	Acrylic
Cyan 9A	2	0	0
Cyan 9B	5	0	0
Cyan 9C	No adhesion	1	1
Cyan 9D	No adhesion	5	4

[00149] The results in Table 19 demonstrate that for monofunctional style inks containing N-vinyl caprolactam, increasing levels of the difunctional monomer 1,6- hexanediol diacrylate resulted in worsening adhesion when incorporated at levels of between 1 and 4%. The adhesion loss is associated with the increased shrinkage that comes from the use of multifunctional monomers.

Example 10 – Properties of cyan ink-jet inks containing diacetone acrylamide and hydroxyopivalyl hydroxypivalate diacrylate multifunctional monomer

[00150] Cyan inkjet inks were prepared according to the formulations in Table 20.

Table 20

Material	Source/commercial code	Examples								
		Cyan 10 A	Cyan 10 B	Cyan 10 C	Cyan 10 D	Cyan 10 E	Cyan 10 F	Cyan 10 G	Cyan 10 H	Cyan 10 I
Diacetone acrylamide	Sigma-Aldrich	24.9	24.9	24.9	24.9	24.9	24.9	24.9	24.9	24.9
hydroxypivalyl hydroxypivalate diacrylate	Miwon , Miramer M210	0	1	2	4	6	8	10	12	15
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	18	17	16	14	12	10	8	6	3
Isobornyl acrylate	Sartomer, SR506D	12	12	12	12	12	12	12	12	12
2-Phenoxyethylacrylate	Sartomer, SR339EU	16.25	16.25	16.25	16.25	16.25	16.25	16.25	16.25	16.25
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2	2	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2	2	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6	6	6	6	6	6
Stabilizer package		1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal acrylate		9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73
Total		**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

Adhesion

[00151] The inks in Table 20 were printed onto Dibond, polycarbonate, and acrylic substrates using a 12 micron K bar and cured at a dose of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. Their adhesion to the test substrates was then tested with the well-known cross hatch adhesion test (ISO 2409) using a scalpel and ISO 2409 adhesive tape from Elcometer. Results are given in numerical categories according to the amount of ink removed from zero (perfect, no ink removed) to 5 (>35% ink removed). Inks where all the ink is removed and there is no adhesion at all are also recorded. These results are given in Table 21.

Table 21

Example	Crosshatch adhesion test results		
	Dibond	Polycarbonate	Acrylic
Cyan 10 A	2	0	0
Cyan 10 B	5	1	1
Cyan 10 C	4	1	0
Cyan 10 D	4	1	0
Cyan 10 E	No adhesion	4	1
Cyan 10 F	No adhesion	No adhesion	2
Cyan 10 G	No adhesion	No adhesion	4
Cyan 10 H	No adhesion	No adhesion	No adhesion
Cyan 10 I	No adhesion	No adhesion	No adhesion

[00152] The results in Table 21 demonstrate that for monofunctional style inks containing diacetone acrylamide, increasing levels of the difunctional monomer hydroxypivalyl hydroxypivalate diacrylate leads to worsening adhesion when incorporated at levels of between 1-10% depending on the substrate, and total adhesion loss above 10%. When compared directly with the results of Example 8 it is clear that diacetone acrylamide offers a close performance profile to N-vinylcaprolactam and that adhesion loss is associated with the increased shrinkage that comes from the use of the multifunctional monomer hydroxypivalyl hydroxypivalate diacrylate.

Example 11– Properties of cyan ink-jet inks containing diacetone acrylamide and 1,6-hexanediol multifunctional monomer

[00153] Cyan inkjet inks were prepared according to the formulations in Table 22.

Table 22

Material	Source/commercial code	Examples			
		Cyan 11 A	Cyan 11 B	Cyan 11 C	Cyan 11 D
Diacetone acrylamide	Sigma-Aldrich	24.9	24.9	24.9	24.9
1,6-hexanediol diacrylate	Allnex, HDDA	0	1	2	4
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	18	17	16	14
Isobornyl acrylate	Sartomer, SR506D	12	12	12	12

Material	Source/commercial code	Examples			
		Cyan 11 A	Cyan 11 B	Cyan 11 C	Cyan 11 D
2-Phenoxyethylacrylate	Sartomer, SR339EU	16.25	16.25	16.25	16.25
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6
Stabilizer package		1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal acrylate		9.73	9.73	9.73	9.73
Total		**100**	**100**	**100**	**100**

Adhesion

[00154] The inks in Table 22 were printed onto Dibond, polycarbonate, and acrylic substrates using a 12 micron K bar and cured at a dose of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. Their adhesion to the test substrates was then tested with the well-known cross hatch adhesion test (ISO 2409) using a scalpel and ISO 2409 adhesive tape from Elcometer. Results are given in numerical categories according to the amount of ink removed from zero (perfect, no ink removed) to 5 (>35% ink removed). Inks where all the ink is removed and there is no adhesion at all are also recorded. These results are given in Table 23.

Table 23

Example	Crosshatch adhesion test results		
	Dibond	Polycarbonate	Acrylic
Cyan 11 A	No adhesion	0	0
Cyan 11 B	No adhesion	1	0
Cyan 11 C	No adhesion	4	1
Cyan 11 D	No adhesion	No adhesion	5

[00155] The results in Table 23 demonstrate that for monofunctional style inks containing diacetone acrylamide, increasing levels of the difunctional monomer 1,6- hexanediol

diacrylate leads to worsening adhesion when incorporated at levels of between 1 and 4%. When compared directly with the results of Example 9 it is clear that diacetone acrylamide offers a close performance profile to N-vinylcaprolactam and that adhesion loss is associated with the increased shrinkage that comes from the use of the multifunctional monomer 1,6-hexanediol diacrylate.

Example 12 – Properties of cyan ink-jet inks containing diacetone acrylamide and trimethylolpropane triacrylate multifunctional monomer

[00156] Cyan inkjet inks were prepared according to the formulations in Table 24.

Table 24

Material	Source/commercial code	Examples								
		Cyan 12 A	Cyan 12 B	Cyan 12 C	Cyan 12 D	Cyan 12 E	Cyan 12 F	Cyan 12 G	Cyan 12 H	Cyan 12 I
Diacetone acrylamide	Sigma-Aldrich	24.9	24.9	24.9	24.9	24.9	24.9	24.9	24.9	24.9
Trimethylolpropane triacrylate	Sartomer, SR 351	0	1	2	4	6	8	10	12	15
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	18	17	16	14	12	10	8	6	3
Isobornyl acrylate	Sartomer, SR506D	12	12	12	12	12	12	12	12	12
2-Phenoxyethylacrylate	Sartomer, SR339EU	16.25	16.25	16.25	16.25	16.25	16.25	16.25	16.25	16.25
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2	2	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2	2	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6	6	6	6	6	6
Stabilizer package		1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal acrylate		9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73
Total		**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

Adhesion

[00157] The inks in Table 24 were printed onto Dibond, polycarbonate, and acrylic substrates using a 12 micron K bar and cured at a dose of 150 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. Their adhesion to the test substrates was then tested

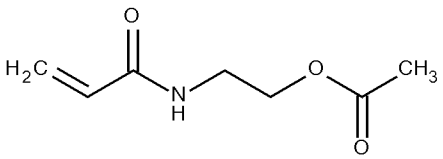
with the well-known cross hatch adhesion test (ISO 2409) using a scalpel and ISO 2409 adhesive tape from Elcometer. Results are given in numerical categories according to the amount of ink removed from zero (perfect, no ink removed) to 5 (>35% ink removed). Inks where all the ink is removed and there is no adhesion at all are also recorded. These results are given in Table 25.

Table 25

Example	Crosshatch adhesion test results		
	Dibond	Polycarbonate	Acrylic
Cyan 12 A	3	0	0
Cyan 12 B	3	1	0
Cyan 12 C	3	4	0
Cyan 12 D	3	4	4
Cyan 12 E	No adhesion	No adhesion	No adhesion
Cyan 12 F	No adhesion	No adhesion	No adhesion
Cyan 12 G	No adhesion	No adhesion	No adhesion
Cyan 12 H	No adhesion	No adhesion	No adhesion
Cyan 12 I	No adhesion	No adhesion	No adhesion

[00158] The results in Table 25 demonstrate that for monofunctional style inks containing diacetone acrylamide, increasing levels of the multifunctional monomer trimethylolpropane triacrylate leads to worsening adhesion when incorporated at levels of between 1-4% depending on the substrate, and total adhesion loss above 4%. When compared with the results of Examples 8-11 it is clear that diacetone acrylamide offers a close performance profile to N-vinylcaprolactam and that adhesion loss is associated with the increased shrinkage that comes from the use of the multifunctional monomer trimethylolpropane triacrylate.

Example 13 – Preparation of 2-(prop-2-enamido)ethyl acetate.



30.0 g of N-hydroxy ethyl acrylamide (0.2606 moles), 26.32 g of triethylamine (0.2606 moles) and 50 ml of dichloromethane were mixed in a two necked round bottomed flask equipped with a stirrer, condenser and nitrogen inlet and outlet. The temperature was reduced to <5°C using an ice/water bath. The mixture was stirred and 20.46 g of acetyl chloride (0.2606 moles) in 20 ml of dichloromethane was added drop wise ensuring the exotherm was controlled throughout (<10°C). Addition was carried out in approximately 2 hours. The mixture was stirred throughout and under a constant flow of nitrogen gas. The mixture was then allowed to warm to room temperature. The mixture was extracted with 2 x 100 ml of 0.1 M hydrochloric acid, 2 x 100 ml of 0.1 M sodium hydroxide and 2 x 100 ml of deionised water. The organics were then dried with anhydrous magnesium sulphate. The magnesium sulphate was removed by filtration and the solvent removed on a rotary evaporator to yield the product.

Product yield 4.8 g (11.72%).

The product was analysed by IR.

IR: carbonyl C=O at 1740 cm^{-1} due to an ester.

Example 14– Properties of cyan ink-jet inks containing 2-(prop-2-enamido)ethyl acetate

[00159] Cyan inkjet inks were prepared according to the formulations in Table 26. Ink viscosity was recorded using a Brookfield DVII viscometer at 50°C.

Table 26

Material	Source/commercial code	Examples					
		Cyan A (comp)	Cyan B (comp)	Cyan C (inv)	Cyan D (inv)	Cyan E (inv)	Cyan F (inv)
N-vinyl caprolactam	BASF, V-CAP	24.9	0	0	0	0	0
Example 13		0	0	5	10	20	30
Cyclic trimethylolpropane formal acrylate	Sartomer, SR531	23.13	35.575	33.075	30.575	25.575	20.575
2-Phenoxyethylacrylate	Sartomer, SR339EU	23.12	35.575	33.075	30.575	25.575	20.575
Photoinitiator	IGM, Omnirad TPO	4.9	4.9	4.9	4.9	4.9	4.9
Photoinitiator	BASF, Irgacure 184	2	2	2	2	2	2
Photoinitiator	Lambson, DETX	2	2	2	2	2	2
Photoinitiator	BASF, Irgacure 819	2.6	2.6	2.6	2.6	2.6	2.6
Slip additive	Evonik, Tegoglide 410	0.5	0.5	0.5	0.5	0.5	0.5

Material	Source/commercial code	Examples					
		Cyan A (comp)	Cyan B (comp)	Cyan C (inv)	Cyan D (inv)	Cyan E (inv)	Cyan F (inv)
Resin solution (in monomer)	Lucite, Elvacite 2013	6	6	6	6	6	6
Stabilizer package		1.12	1.12	1.12	1.12	1.12	1.12
Pigment concentrate containing 25% CI Pigment Blue 15:4 in cyclic trimethylolpropane formal		9.73	9.73	9.73	9.73	9.73	9.73
Total							
Viscosity (mPas @ 50°C)		9.45	10.4	12.80	13.60	16.10	18.60

Note: "comp" = Comparative Example; "inv" = Inventive Example

Cure speed/blocking resistance

[00160] The inks in Table 26 were printed onto PE85 white Top Trans label substrate (from Avery Dennison) using a number 2 K bar and cured at a dose of 56 mJ under a medium pressure mercury arc lamp on a Primarc Maxicure UV rig. The prints were then stacked with a piece of blank Incada Excel carton board substrate (reverse side) on top and put under a pressure of 10 tons for 5 seconds in a Specac blocking tester. The cartonboard layer was removed and the level of ink blocking determined by amount of color transferred to the blank substrate using a Spectraflash 600 Spectrophotometer measuring the DL* value through a wide aperture. Lower levels of DL* indicate faster cure speed and better blocking performance due to lower ink transfer. Results are given in Table 27.

Table 27

Example	DL* 56mJ
Cyan A	0.70
Cyan B	3.17
Cyan C	3.25
Cyan D	2.76
Cyan E	2.18
Cyan F	1.51

[00161] The results in Table 27 demonstrate that the inventive inks show improved cure /blocking resistance as the level of the acrylamide Example 13 is increased and demonstrates good utility.

Example 15 – Properties of black water-based UV inks containing acrylamide monomers

[00162] Black water-based UV inkjet inks were prepared according to the formulations in Table 28. Ink viscosity was recorded using a Brookfield DVII viscometer at 32°C.

Table 28

Material	Source/commercial code	Examples							
		A (comp)	B (inv)	C (inv)	D (inv)	E (inv)	F (inv)	G (inv)	H (inv)
UV crosslinkable aqueous polyurethane dispersion	NEORAD R-444, ex DSM	20	20	20	20	20	20	20	20
Deionised water		51	46	50	46	46	46	46	46
Solvent	Brenntag UK, Mono propylene glycol	15	15	15	15	15	15	15	15
Photoinitiator	Irgacure 2959, BASF	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Amine synergist	IMHOFF & STAHL GMBH, Triethanolamine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Diacetone acrylamide	DSM Fine Chemicals		5						
N,N-Methylene bisacrylamide	MBA, MRC Unitec			1*					
N-isobutoxy methyl acrylamide	IBMA, MRC Unitec				5				
N-acryloyl morpholine	ACMO, RAHN					5			
N-hydroxy ethyl acrylamide	Sigma-Aldrich						5		
N,N'-diethyl acrylamide	Sigma-Aldrich							5	
N-isopropyl acrylamide	Sigma-Aldrich								5
Black pigment dispersion	SunChemical proprietary	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Biocide	CHEMLINK SPECIALITIES, Nipacide B1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Surfactant	Alpha Chemicals, Capstone FS-3100	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

Material	Source/commercial code	Examples							
		A (comp)	B (inv)	C (inv)	D (inv)	E (inv)	F (inv)	G (inv)	H (inv)
Total		100	100	100	100	100	100	100	100
Viscosity (mPas @ 32°C)		2.37	2.88	2.43	2.88	2.67	2.73	2.88	2.91

Note: "comp" = Comparative Example; "inv" = Inventive Example

* *N,N-Methylene bisacrylamide not sufficiently soluble to be tested at 5%*

Cure speed/resistance

[00163] The inks in Table 28 were printed onto coated Lenetta charts (from Cornelius) using a 10 micron K bar from RK and dried using a hot air blower for 15 seconds to remove all the solvent and giving a dry, tack- free film. This ink film was then cured at a dose of 150 mJ using a 300 W/inch medium pressure mercury arc lamp fitted to a Primarc Maxicure UV curing rig. The resistance of the cured ink was then assessed by a solvent rub test using a Satra STM421 rub tester with the pad soaked in deionised water. The test involves the rub tester moving the sample stage back and forth, and the number of rubs recorded when the sample is showing multiple defects across the entire sample. Results are shown in Table 29 as an average of 2 runs.

Table 29

Example	Water rub resistance at 150 mJ
Comp. A	47
Inv. B	>200
Inv. C	147
Inv. D	141
Inv. E	53
Inv. F	90
Inv. G	102
Inv. H	113

[00164] The results in Table 29 demonstrate that the inventive inks show various degrees of improved cure/resistance as a result of incorporation of acrylamide monomer. The preferred diacetone acrylamide (Inv. B) exhibits better cure/ resistance properties than the other acrylamides tested, including the well-known and widely used tertiary acrylamide ACMO. The invention therefore shows excellent utility in aqueous UV curing Inkjet inks.

Example 16 – Properties of yellow, magenta, and cyan water-based UV inks containing acrylamide monomers

[00165] Yellow, magenta, and cyan water-based UV inkjet inks were prepared according to the formulations in Table 30 using each of 2 different acrylamides:

Diacetone acrylamide (Sigma-Aldrich)

N-isobutoxymethyl acrylamide (MRC Unitec)

Table 30

Material	Source/commercial code	Examples								
		A (comp)	B (inv)	C (inv)	D (comp)	E (inv)	F (inv)	G (comp)	H (inv)	I (inv)
UV crosslinkable aqueous polyurethane dispersion	NEORAD R-444, ex DSM	20	20	20	20	20	20	20	20	20
Deionised water		51	46	46	51	46	46	51	46	46
Solvent	Brenntag UK, Mono propylene glycol	15	15	15	15	15	15	15	15	15
Photoinitiator	Irgacure 2959, BASF	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Amine synergist	IMHOFF & STAHL GMBH, Triethanolamine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Diacetone acrylamide	DSM Fine Chemicals		5			5			5	
N-isobutoxy methyl acrylamide	IBMA, MRC Unitec			5			5			5
Yellow pigment dispersion	SunChemical proprietary	12.5	12.5	12.5						
Magenta pigment dispersion	SunChemical proprietary				12.5	12.5	12.5			
Cyan pigment dispersion	SunChemical proprietary							12.5	12.5	12.5
Biocide	CHEMLINK SPECIALITIES, Nipacide B1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Surfactant	Alpha Chemicals, Capstone FS-3100	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Total		100	100	100	100	100	100	100	100	100

Note: "comp" = Comparative Example; "inv" = Inventive Example

Cure speed/resistance

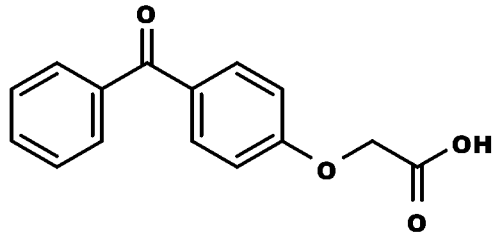
[00166] The inks in Table 30 were printed onto coated Lenetta charts (from Cornelius) using a 10 micron K bar from RK and dried using a hot air blower for 15 seconds to remove all the solvent and giving a dry, tack- free film. This ink film was then cured at a dose of either 31 or 41 mJ using a 300 W/inch medium pressure mercury arc lamp fitted to a Primarc Maxicure UV curing rig. The resistance of the cured ink was then assessed by a solvent rub test using a Satra STM421 rub tester with the pad soaked in deionised water. The test involves the rub tester moving the sample stage back and forth, and the number of rubs recorded when the sample is showing multiple defects across the entire sample. Results are shown in Table 31 as an average of 2 runs.

Table 31

Example	Water rub resistance at 41 mJ	Water rub resistance at 31 mJ
Comp. A	>200	>200
Inv. B	>200	>200
Inv. C	>200	>200
Comp. D	79	-
Inv. E	>200	-
Inv. F	>200	-
Comp. G	44	-
Inv. H	26	-
Inv. I	>200	-

[00167] The results in Table 31 demonstrate that the inventive inks show various degrees of improved cure/resistance as a result of incorporation of acrylamide monomer. The preferred diacetone acrylamide (Inv. B, E & H) exhibits excellent utility in magenta inks, but shows no significant change in cyan inks. N-isobutyl methyl acrylamide (Inv. C, F & I) on the other hand shows excellent utility in yellow and cyan inks. The resistance of standard yellow inks and those containing acrylamide monomer all demonstrate cure speeds sufficient to give >200 rubs at even the lowest dose capable of being tested and thus good utility is implied.

Example 17 – Preparation of 4-carboxymethoxy benzophenone



[00168] 79.2 g (0.4 moles) of 4-hydroxy benzophenone , 82.9 g potassium carbonate (0.6 moles) and 400 mL of methyl ethyl ketone were mixed in a 2 L flask equipped with a stirrer, temperature probe and condenser. The mixture was heated to reflux for 1 hour. After cooling to room temperature, 73.5 g (0.6 moles) ethyl chloroacetate was added and the mixture heated to reflux for a total of 10.25 hours before cooling and adding 400 mL of water. The methyl ethyl ketone was distilled off and cooled to 60°C before adding a solution of 32.5 g sodium hydroxide in 800 mL of water. The solution was heated again to reflux for 3 hours before cooling to 95°C and adding 120 mL of concentrated hydrochloric acid over 10-20 minutes, keeping the reaction temperature at 95°C +/-2°C. The solution was refluxed for 5 minutes before cooling and leaving to stand overnight. The solution was filtered and washed with 500 mL deionised water before drying in a vacuum oven to obtain the final product.

Yield 101.09 g (98.7% %).

Example 18 – Properties of cyan water-based UV inks containing acrylamide monomers

[00169] Cyan water-based UV inkjet inks were prepared according to the formulations in Table 32 using diacetone acrylamide and each of 3 different photoinitators:

Polyethylene glycol mono-4-(2-hydroxy-2-methyl propiophenone) ether (PC3221, Inspec UK, Southampton)

4-hydroxy benzophenone (Sigma Aldrich)

4-carboxymethoxy benzophenone (Example 17)

Table 32

Material	Source/commercial code	Examples					
		A (comp)	B (inv)	C (comp)	D (inv)	E (comp)	F (inv)
UV crosslinkable aqueous polyurethane dispersion	NEORAD R-444, ex DSM	20	20	20	20	20	20
Deionised water		51	46	51	46	51	46
Solvent	Brenntag UK, Mono propylene glycol	15	15	15	15	15	15
PC3221	Inspec	1.0	1.0				
4-hydroxy benzophenone	Sigma-Aldrich			0.5	0.5		
Example 17						0.5	0.5
Amine synergist	IMHOFF & STAHL GMBH, Triethanolamine	0.1	0.1	1.0	1.0	1.0	1.0
Diacetone acrylamide	DSM Fine Chemicals		5		5		5
Cyan pigment dispersion	SunChemical proprietary					12.5	12.5
Biocide	CHEMLINK SPECIALITIES, Nipacide B1	0.1	0.1	0.1	0.1	0.1	0.1
Surfactant	Alpha Chemicals, Capstone FS-3100	0.3	0.3	0.3	0.3	0.3	0.3
Total		100	100	100	100	100	100

Note: "comp" = Comparative Example; "inv" = Inventive Example

Cure speed/resistance

[00170] The inks in Table 32 were printed onto coated Lenetta charts (from Cornelius) using a 10 micron K bar from RK and dried using a hot air blower for 15 seconds to remove all the solvent and giving a dry, tack- free film. This ink film was then cured at a dose of either 42 or 113 mJ using a 300 W/inch medium pressure mercury arc lamp fitted to a Primarc Maxicure UV curing rig. The resistance of the cured ink was then assessed by a solvent rub test using a Satra STM421 rub tester with the pad soaked in deionised water. The test involves the rub tester moving the sample stage back and forth, and the number of rubs recorded when the sample is showing multiple defects across the entire sample. Results are shown in Table 33 as an average of 2 runs.

Table 33

Example	Water rub resistance at 113 mJ	Water rub resistance at 42 mJ
Comp. A	-	38
Inv. B	-	>200
Comp. C	8	-
Inv. D	>200	-
Comp. E	63	-
Inv. F	>200	-

[00171] The results in Table 33 demonstrate that the inventive inks show various degrees of improved cure/resistance as a result of incorporation of acrylamide monomer independently of the type of photoinitiator being used for curing. The preferred diacetone acrylamide demonstrates excellent utility in cyan inks with any of the 3 photoinitiator types evaluated, giving a significant improvement to the cure/resistance properties.

Example 19 – Properties of black water-based UV inks containing acrylamide monomers

[00172] Black water-based UV inkjet inks were prepared according to the formulations in Table 34, using diacetone acrylamide or N,N-methylene bisacrylamide.

Table 34

Material	Source/commercial code	Examples		
		A (comp)	B (inv)	C (inv)
UV crosslinkable aqueous polyurethane dispersion	NEORAD R-448, ex DSM	50	45	45
Deionised water		23.5	26.5	26.5
Photoinitiator	Irgacure 2959, BASF	1.0	1.0	1.0
Amine synergist	Amietol M12 ex Taminco,	0.4	0.4	0.4
Diacetone acrylamide	DSM Fine Chemicals		2.0	
N,N-Methylene bisacrylamide	MBA, MRC Unitec			2.0
Black pigment dispersion	Cabojet 250C, CABOT	25	25	25

Material	Source/commercial code	Examples		
		A (comp)	B (inv)	C (inv)
Biocide	CHEMLINK SPECIALITIES, Nipacide B1	0.1	0.1	0.1
Total		100	100	100

Note: "comp" = Comparative Example; "inv" = Inventive Example

Cure speed/resistance

[00173] The inks in Table 34 were printed onto coated Melinex 752 polyester substrate from DuPont using an 8 micron K bar from RK and dried using a hot air blower for 10 seconds to remove all the solvent and giving a dry, tack- free film. This ink film was then cured at a dose of 200 mJ using a Fusion UV curing rig fitted with an "H" bulb.

[00174] The resistance of the cured ink was then assessed by a series of tests:

- Solvent resistance, measured as number of double rubs of a cotton bud soaked in methyl ethyl ketone to penetrate the ink through to the substrate
- Scratch resistance, a qualitative assessment based on the ability of the cured ink to resist scratching by finger nail and given a rating between 1 (poor) to 10 (no defect)
- Face-to-face block resistance, where a 45 cm^2 area of ink film was blocked to itself under a pressure of 5 kg for 1 minute. The degree of tack between the blocked ink layers was determined as 1 (the ink films block/stick to each other) to 10 (no tack observed between the two layers.
- Face-to-back block resistance, where a 45 cm^2 area of ink film was blocked to a blank piece of Melinex 752 substrate under a pressure of 5 kg for one minute. The degree of tack between the blocked ink layer and the blank substrate was determined as 1 (the ink film blocks/sticks to the blank substrate) to 10 (no tack observed between the two layers).

Table 35

Example	MEK Solvent resistance at 200 mJ	Scratch resistance at 200 mJ	Face-to-face block resistance	Face-to-back block resistance
Comp. A	40	9	8	9
Inv. B	>100	9	9	10
Inv. C	>100	10	10	10

[00175] The results in Table 35 demonstrate that the inventive inks show improved cure/resistance as a result of incorporation of acrylamide monomer and therefore have excellent utility in water-based inkjet inks

[00176] The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements on this invention that fall within the scope and spirit of the invention.

CLAIMS

What is claimed is:

1. A digital printing ink comprising:
   a) 1-60 wt% of an acrylamide material or blends thereof;
   b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
   c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
   d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
   e) 0.1-25 wt% of a photoinitiator or blends thereof;
   f) 0-18 wt% of an amine synergist;
   g) 0-5 wt% of N-vinyl compounds; and
   h) 0-70 wt% water;

   wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

2. A digital printing ink comprising:
   a) 1-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
   b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
   c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
   d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
   e) 0.1-25 wt% of a photoinitiator or blends thereof;
   f) 0-18 wt% of an amine synergist;
   g) 0-5 wt% of N-vinyl compounds; and
   h) 0-70 wt% water;

   wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

3. The ink of claim 1 or claim 2, wherein the acrylamide material is selected from the group consisting of diacetone acrylamide, N-isobutoxymethyl acrylamide, N-isopropyl acrylamide, N,N'-methylene bisacrylamide, or 2-(prop-2-enamido)ethylacetate, or a combination thereof.

4. The ink of claim 1 or claim 2, wherein the majority of the acrylamide material is diacetone acrylamide.

5. The ink of claim 1 or claim 2, wherein all of the acrylamide material comprises diacetone acrylamide.

6. The ink of claim 1 or claim 2, wherein the monofunctional acrylate monomer, or blends thereof, comprises no more than 25 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

7. The ink of claim 1 or claim 2, wherein the monofunctional monomer, or blends thereof, comprises 0.1-20 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate and 3,3,5-trimethyl cyclohexyl acrylate.

8. The ink of claim 1 or claim 2, wherein the monofunctional monomer, or blends thereof, comprises 0.1-10 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

9. The ink of claim 1 or claim 2, wherein the monofunctional monomer, or blends thereof, comprises 0.1-5 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

10. The ink of claim 1 or claim 2, wherein the monofunctional monomer, or blends thereof, contains no isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

11. The ink of claim 1 or claim 2, containing no N-vinyl compounds.

12. The ink of claim 1 or claim 2, containing no difunctional or higher monomers.

13. The ink of claim 1 or claim 2, wherein the photoinitiator is present in an amount of 0.1-20 wt%.

14. The ink of claim 1 or claim 2, wherein the water is present in an amount of 20-70 wt%.

15. The ink of claim 1 or claim 2, wherein the acrylamide material is present in an amount of 1-40 wt%.

16. The ink of claim 1 or claim 2, wherein the acrylamide material is present in an amount of 1-30 wt%.

17. The ink of claim 1 or claim 2, wherein the acrylamide material is present in an amount of 1-20 wt%.

18. The ink of claim 1 or claim 2, wherein the acrylamide material is present in an amount of 1-10 wt%.

19. The ink of claim 1 or claim 2, wherein the acrylamide material is present in an amount of 1-5 wt%.

20. The ink of any one of claims 1-19, further comprising a colorant.

21. The ink of any one of claims 1-20, further comprising one or more additives selected from the group consisting of stabilizers, surfactants, defoamers, slip additives, wetting additives and synergists.

22. An ink according to any of the previous claims, wherein the ink is an ink jet ink.

23. An ink according to any of the previous claims, wherein the ink is an aerosol jet ink.

24. A method of making a digital ink, comprising mixing:
    a) 1-60 wt% of an acrylamide material or blends thereof;
    b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
    c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
    d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;

e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

25. A method of making a digital ink, comprising mixing:
a) 1-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
c) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
d) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
e) 0.1-25 wt% of a photoinitiator or blends thereof;
f) 0-18 wt% of an amine synergist;
g) 0-5 wt% of N-vinyl compounds; and
h) 0-70 wt% water;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

26. Use of the digital ink of any one of claims 1-23, comprising printing the ink onto a substrate.

27. A printed article comprising the digital ink of any one of claims 1-23.

28. A water-based digital printing ink comprising:
a) 0.5-60 wt% of an acrylamide material or blends thereof;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;

h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

29. A water-based digital printing ink comprising:
a) 0.5-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
b) 15-50 wt% of an acrylated polyurethane dispersion;
c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
f) 0.1-25 wt% of a photoinitiator or blends thereof;
g) 0-18 wt% of an amine synergist;
h) 0-5 wt% of N-vinyl compounds;
i) 1-80 wt% water; and
j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

30. The ink of claim 28 or 29, wherein the acrylamide material is selected from the group consisting of diacetone acrylamide, N-isobutoxymethyl acrylamide, N-isopropyl acrylamide, N,N'-methylene bisacrylamide, or 2-(prop-2-enamido)ethylacetate, or a combination thereof.

31. The ink of claim 28 or claim 29, wherein the majority of the acrylamide material is diacetone acrylamide.

32. The ink of claim 28 or claim 29, wherein all of the acrylamide material is diacetone acrylamide.

33. The ink of claim 28 or 29, wherein the monofunctional acrylate monomer, or blends thereof, comprises no more than 25 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

34. The ink of claim 28 or claim 29, wherein the monofunctional monomer, or blends thereof, comprises 0.1-20 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate and 3,3,5-trimethyl cyclohexyl acrylate.

35. The ink of claim 28 or claim 29, wherein the monofunctional monomer, or blends thereof, comprises 0.1-10 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

36. The ink of claim 28 or claim 29, wherein the monofunctional monomer, or blends thereof, comprises 0.1-5 wt% of isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

37. The ink of claim 28 or claim 29, wherein the monofunctional monomer, or blends thereof, contains no isobornyl acrylate, *t*-butyl cyclohexyl acrylate or 3,3,5-trimethyl cyclohexyl acrylate.

38. The ink of claim 28 or claim 29, wherein the acrylated polyurethane dispersion is present in an amount of 20-30 wt%.

39. The ink of claim 28 or claim 29, containing no N-vinyl compounds.

40. The ink of claim 28 or claim 29, containing no difunctional or higher monomers.

41. The ink of claim 28 or claim 29, wherein the photoinitiator is present in an amount of 0.1-20 wt%.

42. The ink of claim 28 or claim 29, wherein the water is present in an amount of 20-80 wt%.

43. The ink of claim 28 or claim 29, wherein the water is present in an amount of 60-70 wt%.

44. The ink of claim 28 or claim 29, wherein the water is present in an amount of 30-70 wt%.

45. The ink of claim 28 or claim 29, wherein the water is present in an amount of 40-50 wt%.

46. The ink of claim 28 or claim 29, wherein the water is present in an amount of 20-30 wt%.

47. The ink of claim 28 or claim 29, wherein the solvent is present in an amount of 1-30 wt%.

48. The ink of claim 28 or claim 29, wherein the solvent is present in an amount of 1-20 wt%.

49. The ink of claim 28 or claim 29, wherein the acrylamide material is present in an amount of 0.5-40 wt%.

50. The ink of claim 28 or claim 29, wherein the acrylamide material is present in an amount of 0.5-30 wt%.

51. The ink of claim 28 or claim 29, wherein the acrylamide material is present in an amount of 0.5-20 wt%.

52. The ink of claim 28 or claim 29, wherein the acrylamide material is present in an amount of 0.5-10 wt%.

53. The ink of claim 28 or claim 29, wherein the acrylamide material is present in an amount of 0.5-5 wt%.

54. The ink of any one of claims 28-53, further comprising a colorant.

55. The ink of any one of claims 28-54, further comprising one or more additives selected from the group consisting of stabilizers, surfactants, defoamers, slip additives, wetting additives and synergists.

56. An ink according to any one of claims 28-55, wherein the ink is an ink jet ink.

57. An ink according to any one of claims 28-55, wherein the ink is an aerosol jet ink.

58. A method of making a water-based digital printing ink comprising mixing:
    a) 0.5-60 wt% of an acrylamide material or blends thereof;
    b) 15-50 wt% of an acrylated polyurethane dispersion;
    c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
    d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
    e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
    f) 0.1-25 wt% of a photoinitiator or blends thereof;
    g) 0-18 wt% of an amine synergist;
    h) 0-5 wt% of N-vinyl compounds;
    i) 1-80 wt% water; and
    j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

59. A method of making a water-based digital printing ink comprising mixing:
    a) 0.5-60 wt% of an acrylamide material or blends thereof, wherein at least a portion of the acrylamide material is diacetone acrylamide;
    b) 15-50 wt% of an acrylated polyurethane dispersion;
    c) 0-80 wt% of a monofunctional acrylate monomer or blends thereof;
    d) 0-10 wt% of a difunctional acrylate monomer or blends thereof;
    e) 0-5 wt% of a trifunctional or higher acrylate monomer or blends thereof;
    f) 0.1-25 wt% of a photoinitiator or blends thereof;
    g) 0-18 wt% of an amine synergist;

h) 0-5 wt% of N-vinyl compounds;

i) 1-80 wt% water; and

j) 0-30 wt% of a water-compatible organic solvent;

wherein the composition contains no N-vinyl caprolactam, N-vinyl pyrrolidone, or N-acryloyl morpholine.

60. Use of the digital ink of any one of claims 28-57, comprising printing the ink onto a substrate.

61. A printed article comprising the digital ink of any one of claims 28-57.

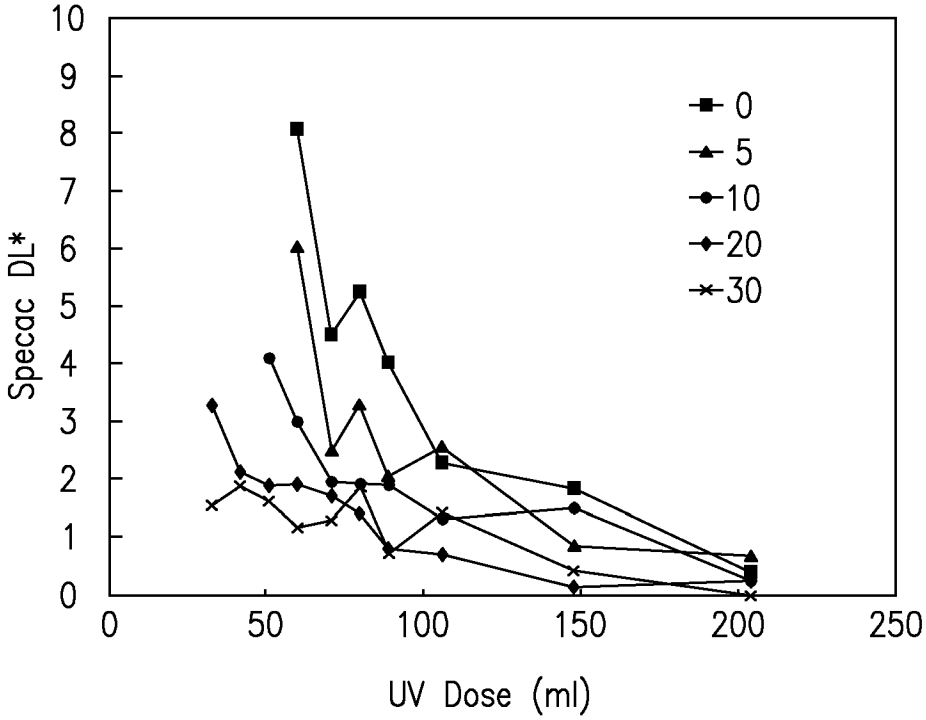


FIG. 1

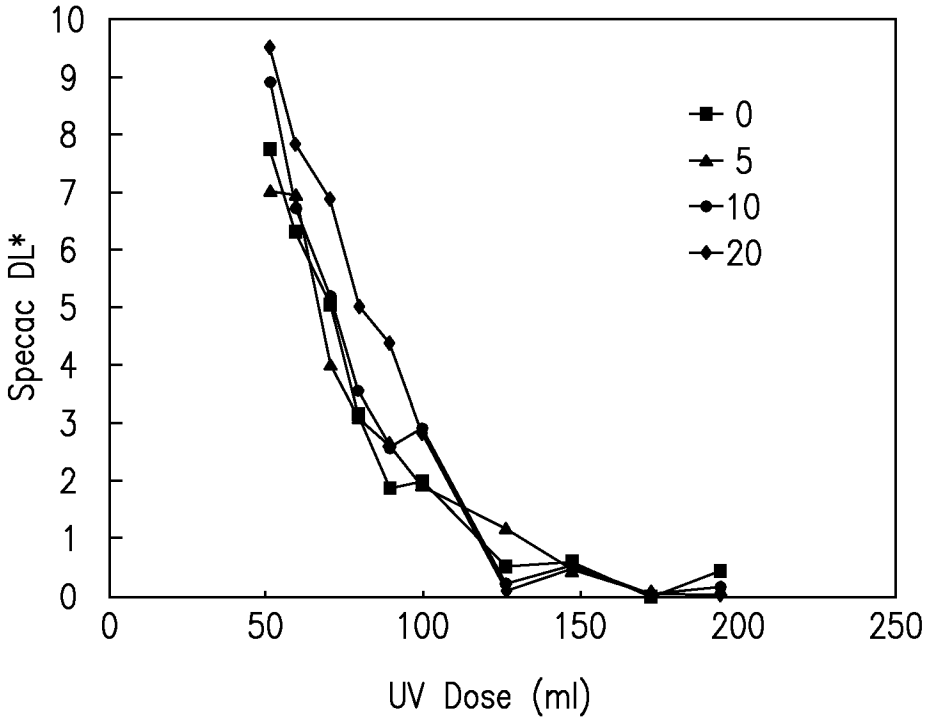


FIG. 2

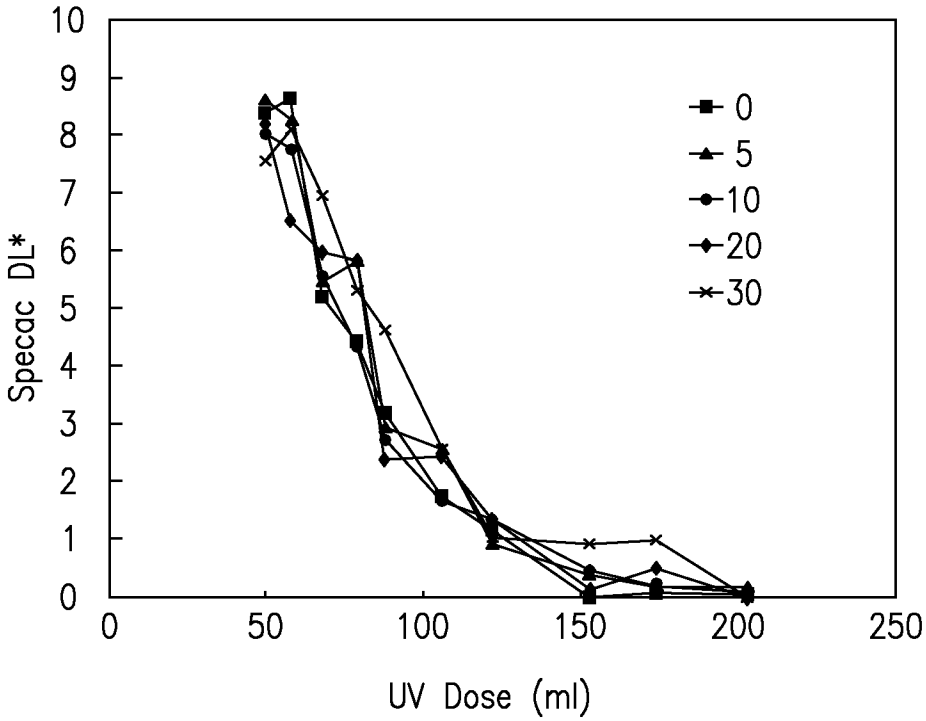

10
9
8
7
6
5
4
3
2
1
0
Specac DL*
0
50
100
150
200
250
UV Dose (ml)
0
5
10
20
30

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/17952

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C09D 11/322, 11/30 (2015.01)
CPC - C09D 11/322, 11/30
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)
IPC(8): C09D 11/322, 11/30 (2015.01)
CPC: C09D 11/322, 11/30

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)
PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); ProQuest; Scifinder; Google/Google Scholar; KEYWORDS: digital, ink, acrylamide, photoinitiator, diacetone, water, polyurethane, dispersion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2004/0085418 A1 (YAU, HL et al.) 06 May 2004; paragraphs [0020], [0071]-[0073]	1-2, 3/1-2, 4/1-2, 5/1-2, 6/1-2, 7/1-2, 8/1-2, 9/1-2, 10/1-2, 11/1-2, 12/1-2, 13/1-2, 14/1-2, 15/1-2, 16/1-2, 17/1-2, 18/1-2, 19/1-2, 24-25, 28-29, 30/28-29, 31/28-29, 32/28-29, 33/28-29, 34/28-29, 35/28-29, 36/28-29, 37/28-29, 38/28-29, 39/28-29, 40/28-29, 41/28-29, 42/28-29, 43/28-29, 44/28-29, 45/28-29, 46/28-29, 47/28-29, 48/28-29, 49/28-29, 50/28-29, 51/28-29, 52/28-29, 53/28-29, 58-59

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 April 2015 (26.04.2015)	29 MAY 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/17952

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/0148924 A1 (LACHOWICZ, A et al.) 06 July 2006; paragraphs [0074], [0078]-[0079]	1-2, 3/1-2, 4/1-2, 5/1-2, 6/1-2, 7/1-2, 8/1-2, 9/1-2, 10/1-2, 11/1-2, 12/1-2, 13/1-2, 14/1-2, 15/1-2, 16/1-2, 17/1-2, 18/1-2, 19/1-2, 24-25, 28-29, 30/28-29, 31/28-29, 32/28-29, 33/28-29, 34/28-29, 35/28-29, 36/28-29, 37/28-29, 38/28-29, 39/28-29, 40/28-29, 41/28-29, 42/28-29, 43/28-29, 44/28-29, 45/28-29, 46/28-29, 47/28-29, 48/28-29, 49/28-29, 50/28-29, 51/28-29, 52/28-29, 53/28-29, 58-59
Y	US 2012/0270018 A1 (MIZUTANI, S et al.) 25 October 2012; claim 2	6/1-2, 7/1-2, 8/1-2, 9/1-2, 10/1-2, 33/28-29, 34/28-29, 35/28-29, 36/28-29, 37/28-29
Y	US 2014/0011941 A1 (ANTON, WL et al.) 09 January 2014; paragraphs [0150]-[0151]	28-29, 30/28-29, 31/28-29, 32/28-29, 33/28-29, 34/28-29, 35/28-29, 36/28-29, 37/28-29, 38/28-29, 39/28-29, 40/28-29, 41/28-29, 42/28-29, 43/28-29, 44/28-29, 45/28-29, 46/28-29, 47/28-29, 48/28-29, 49/28-29, 50/28-29, 51/28-29, 52/28-29, 53/28-29, 58-59
Y	US 2011/0168053 A1 (PENG, X et al.) 14 July 2011; claim 9	46/28-29
A	US 2009/0087626 A1 (HAYATA, Y et al.) 02 April 2009; entire document	1-2, 3/1-2, 4/1-2, 5/1-2, 6/1-2, 7/1-2, 8/1-2, 9/1-2, 10/1-2, 11/1-2, 12/1-2, 13/1-2, 14/1-2, 15/1-2, 16/1-2, 17/1-2, 18/1-2, 19/1-2, 24-25, 28-29, 30/28-29, 31/28-29, 32/28-29, 33/28-29, 34/28-29, 35/28-29, 36/28-29, 37/28-29, 38/28-29, 39/28-29, 40/28-29, 41/28-29, 42/28-29, 43/28-29, 44/28-29, 45/28-29, 46/28-29, 47/28-29, 48/28-29, 49/28-29, 50/28-29, 51/28-29, 52/28-29, 53/28-29, 58-59

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/17952

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

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

3. ☒ Claims Nos.: 20-23, 26-27, 54-57, 60-61
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.