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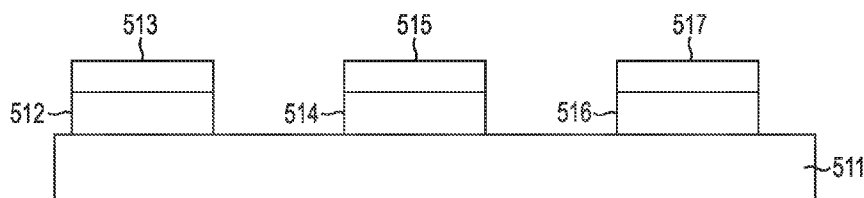


Fig. 5

(57) Abstract: Liquid jet or aerosol jet coating compositions, particularly metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, or a metal closure) liquid jet or aerosol jet coating compositions, coated metal substrates, metal packaging, and methods - methods of coating a metal substrate, and methods of making a metal packaging container (e.g., a food, beverage, or aerosol can), a portion thereof, or a metal closure for a container.

METAL PACKAGING LIQUID OR AEROSOL JET COATING
COMPOSITIONS, COATED SUBSTRATES, PACKAGING, AND METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. Provisional Application Serial No. 63/190,754, filed on May 19, 2021, which is incorporated herein by reference.

BACKGROUND

A wide variety of liquid applied coating compositions have been used to provide hardened coatings on the surfaces of metal packaging articles (e.g., food and beverage cans, metal closures). For example, metal cans are sometimes coated with liquid coating compositions using “coil coating” or “sheet coating” operations, i.e., a planar coil or sheet of a suitable substrate (e.g., steel or aluminum metal) is coated with a suitable liquid coating composition, which is subsequently hardened (e.g., cured). The coated substrate then is formed into the can end or body. Alternatively, liquid coating compositions may be applied (e.g., by spraying, dipping, rolling, etc.) to the formed article and then hardened (e.g., cured) to form a continuous coating.

Metal packaging coatings should preferably be capable of high-speed application to the substrate and provide the necessary properties when hardened to perform in this demanding end use. For example, the hardened coating should preferably be safe for food contact, not adversely affect the taste of the packaged food or beverage product, have excellent adhesion to the substrate, resist staining and other coating defects such as “popping,” “blushing,” and/or “blistering,” and resist degradation over long periods of time, even when exposed to harsh environments. In addition, the hardened coating should generally be capable of maintaining suitable film integrity during can fabrication and be capable of withstanding the processing conditions to which the can may be subjected during product packaging. The hardened coating should also generally be capable of surviving routine can drop events (e.g., from a store shelf) in which the underlying metal substrate is dented, without rupturing or cracking.

Roll and spray applied packaging coatings largely satisfy the needs of the rigid metal packaging market today, but their use leaves significant room for improvement. These coating methods largely result in a monolithic film, which is an all-over coating (i.e., a

coating that covers the entire surface of a substrate) with a single thickness. Using such methods, there is no practical ability to direct the coating composition to only specific locations on the substrate, or to vary the thickness of the coating across the substrate. Traditional coating methods are also labor intensive and potentially expose the operator to hazardous materials, thereby requiring expensive large-scale engineering controls. In addition, roll-applied coil coatings are often formulated with a significant amount of volatile organic content (VOC) to achieve the rheology required for a defect-free application. Finally, traditional coating equipment for this industry is large, complex, and difficult to clean, making coating change-overs expensive and time-consuming.

What is needed is an improved coating composition and method for rigid metal packaging applications, which overcomes the above disadvantages associated with conventional liquid packaging coating compositions and application methods.

SUMMARY

The present disclosure provides liquid jet or aerosol jet coating compositions, particularly metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, or a metal closure) liquid jet or aerosol jet coating compositions, coated metal substrates, metal packaging, and methods – methods of coating a metal substrate, and methods of making a metal packaging container (e.g., a food, beverage, or aerosol can), a portion thereof, or a metal closure for a container.

In one embodiment a metal packaging liquid jet or aerosol jet coating composition is provided that includes: polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons, wherein the polymer particles have a particle size distribution having a D50 of less than 10 microns; and a liquid carrier comprising water in a major amount of the liquid carrier. Methods of coating such compositions on metal substrates to form coated metal substrates, as well as coated metal substrates, are also provided. Methods of using the coated metal substrates to form metal packaging, as well as the metal packaging, are also provided.

Herein, “metal packaging” coating compositions refer to coating compositions that are suitable for coating on rigid metal directly, or indirectly on a pretreatment layer or a primer layer that is not derived from a free-standing film (i.e., a film formed before being applied to another substrate, such as by lamination) overlying a substrate. Metal packaging typically does not include a free-standing plastic film of at least 10 microns thick, paper or other fibrous material, or metal foil, which is then applied (e.g., adhered) to rigid metal

packaging). Thus, by way of example, a liquid jet or aerosol jet composition applied either to a paper layer overlying a metal substrate, or to a laminated plastic layer overlying a metal substrate, is not a metal packaging coating composition as used herein.

A “liquid or aerosol jet coating composition” refers to a composition that includes
5 polymer particles in a water-based carrier, thereby forming a water-based polymer dispersion.

The phrase “metal packaging coating composition” does not imply that metal is necessarily included in the coating composition. That is, the term “metal,” as used in the context of a metal packaging coating composition, refers to the type of packaging and does not require the presence of any metal in the coating composition.

10 A “hardened” coating refers to one wherein particles are covalently cured via a crosslinking reaction (e.g., a thermoset coating) or the particles simply fused and/or coalesced in the absence of a crosslinking reaction (e.g., a thermoplastic coating), and adhered to a metal substrate, thereby forming a coated metal substrate. The term “hardened” does not imply anything related to the relative hardness or softness (T_g) of a coating.

15 An “adherent” coating refers to a hardened coating that adheres (i.e., bonds) to a substrate, such as a metal substrate, preferably according to the Adhesion Test described in the Test Methods. Preferably, an adhesion rating of 9 or 10, preferably 10, is considered to be adherent.

A “continuous” coating refers to a hardened coating that is free of coating defects
20 (preferably, free of pinholes) that result in exposed substrate (i.e., regions of the substrate exposed through the hardened coating). Such film imperfections/failures are preferably indicated by a current flow measured in milliamps (mA) using the Flat Panel Continuity Test described in the Test Methods. For purposes of this application, a continuous coating preferably passes less than 200 mA when evaluated according to this test. A continuous
25 coating may be an all-over coating, completely covering the substrate, or it may only cover parts of the substrate, e.g., as in a patterned coating.

A “patterned” coating (i.e., a multi-portion coating) refers to a hardened coating printed in two or more regions on a substrate surface, which may or may not have “blank” regions between and/or surrounding the printed (i.e., coated) regions, wherein “blank”
30 regions have no coating thereon. A “patterned” coating refers to any coating having one or more of the following: (i) two or more hardened coating portions of a same chemical composition, which are not directly contiguous, disposed on different regions of a same substrate surface and present in a same overall multi-portion coating; (ii) two or more hardened coating portions of different chemical compositions (e.g., having different color,

gloss level, etc.) disposed on different regions of a same substrate surface and present in a same overall multi-portion coating; or (iii) two or more hardened coating portions of a same chemical composition of different thicknesses or textures, which may or may not be directly contiguous, disposed on different regions of a same substrate surface and present in a same overall multi-portion coating. A patterned coating is distinct from an all-over coating (i.e., a conventionally applied liquid or powder coating with substantially uniform/homogeneous coating (with inherent thickness variation resulting from the conventional coating process) that typically covers an entire surface of a substrate). This definition of a patterned coating also excludes: (a) a substrate coated at only the edges; (b) a substrate coated everywhere but the edge; and (c) a coating that does not exhibit any of (i), (ii), or (iii). The patterned coating may include a regular or irregular pattern of coated regions, which may be in a variety of shapes (e.g., stripes, diamonds, squares, circles, ovals). The terms “pattern” and “patterned” does not require any repetition in design elements, although such repetition may be present. The coated regions of the patterned coating are preferably “continuous” as defined above (in the areas intended to be coated by the pattern), in that they are free of pinholes and other coating defects that result in exposed substrate if an underlying coating is not present.

The term “substantially free” of a particular component means that the compositions or hardened coatings of the present disclosure contain less than 1,000 parts per million (ppm) of the recited component, if any. The term “essentially free” of a particular component means that the compositions or hardened coatings of the present disclosure contain less than 100 parts per million (ppm) of the recited component, if any. The term “essentially completely free” of a particular component means that the compositions or hardened coatings of the present disclosure contain less than 10 parts per million (ppm) of the recited component, if any. The term “completely free” of a particular component means that the compositions or hardened coatings of the present disclosure contain less than 20 parts per billion (ppb) of the recited component, if any. The preceding terms of this paragraph when used with respect to a composition or hardened coating that may contain a recited component, if any, means that the composition or hardened coating contains less than the pertinent ppm or ppb maximum threshold for the component regardless of the context of the component in the composition or hardened coating (e.g., regardless of whether the compound is present in unreacted form, in reacted form as a structural unit of another material, or a combination thereof).

The term “bisphenol” refers to a polyhydric polyphenol having two phenylene groups that each include six-carbon rings and a hydroxyl group attached to a carbon atom of the ring, wherein the rings of the two phenylene groups do not share any atoms in common. By way of

example, hydroquinone, resorcinol, catechol, and the like are not bisphenols because these phenol compounds only include one phenylene ring.

The term “food-contact surface” refers to a surface of an article (e.g., a food or beverage can) intended for prolonged contact with food product. When used, for example, in the context of a metal substrate of a food or beverage container (e.g., can), the term generally refers to an interior metal surface of the container that would be expected to contact food or beverage product in the absence of liquid or aerosol coating composition applied thereon. By way of example, a base layer, intermediate layer, and/or polymer top-coat layer applied on an interior surface of a metal food or beverage can is considered to be applied on a food-contact surface of the can.

The term “on,” when used in the context of a coating applied on a surface or substrate, includes both coatings applied directly (e.g., virgin metal or pre-treated metal such as electroplated steel) or indirectly (e.g., on a primer layer) to the surface or substrate. Thus, for example, a coating applied to a pre-treatment layer (e.g., formed from a chrome or chrome-free pretreatment) or a primer layer overlying a substrate constitutes a coating applied on (or disposed on) the substrate.

The terms “polymer” and “polymeric material” include, but are not limited to, organic homopolymers, copolymers, such as for example, block, graft, random and alternating copolymers, terpolymers, etc., and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term “polymer” shall include all possible geometrical configurations of the material. These configurations include, but are not limited to, isotactic, syndiotactic, and atactic symmetries.

The term “aryl group” (e.g., an arylene group) refers to a closed aromatic ring or ring system such as phenylene, naphthylene, biphenylene, fluorenylene, and indenyl, as well as heteroarylene groups (e.g., a closed aromatic or aromatic-like ring hydrocarbon or ring system in which one or more of the atoms in the ring is an element other than carbon (e.g., nitrogen, oxygen, sulfur, etc.)). Suitable heteroaryl groups include furyl, thienyl, pyridyl, quinolinyl, isoquinolinyl, indolyl, isoindolyl, triazolyl, pyrrolyl, tetrazolyl, imidazolyl, pyrazolyl, oxazolyl, thiazolyl, benzofuranyl, benzothiophenyl, carbazolyl, benzoxazolyl, pyrimidinyl, benzimidazolyl, quinoxalinyl, benzothiazolyl, naphthyridinyl, isoxazolyl, isothiazolyl, purinyl, quinazolinyl, pyrazinyl, 1-oxidopyridyl, pyridazinyl, triazinyl, tetrazinyl, oxadiazolyl, thiadiazolyl, and so on. When such groups are divalent, they are typically referred to as “arylene” or “heteroarylene” groups (e.g., furylene, pyridylene, etc.).

The term “phenylene” as used herein refers to a six-carbon atom aryl ring (e.g., as in a benzene group) that can have any substituent groups (including, e.g., halogens (which are not preferred), hydrocarbon groups, oxygen atoms, hydroxyl groups, etc.). Thus, for example, the following aryl groups are each phenylene rings: $-\text{C}_6\text{H}_4-$, $-\text{C}_6\text{H}_3(\text{CH}_3)-$, and $-\text{C}_6\text{H}(\text{CH}_3)_2\text{Cl}-$.

5 In addition, for example, each of the aryl rings of a naphthalene group are phenylene rings.

The term “multiple” or “multi” means two or more of the referenced item (e.g., material, component, composition, coating portion).

In the context of liquid or aerosol jet coating compositions, “different” means that the liquid or aerosol coating compositions are different (i.e., dissimilar) in one or more
10 chemical/physical ways (e.g., monomer types/amounts, molecular weight of polymer particles, color of coating composition, additive types/amounts) thereby providing one or more different functions (e.g., hardness, flexibility, corrosion resistance, aesthetic, tactile).

Herein, the term “comprises” and variations thereof do not have a limiting meaning where these terms appear in the description and embodiments. Such terms will be understood
15 to imply the inclusion of a stated step or element or group of steps or elements but not the exclusion of any other step or element or group of steps or elements. By “consisting of” is meant including, and limited to, whatever follows the phrase “consisting of.” Thus, the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present. By “consisting essentially of” is meant including any
20 elements listed after the phrase, and limited to other elements that do not interfere with or contribute to the activity or action specified in the disclosure for the listed elements. Thus, the phrase “consisting essentially of” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present depending upon whether or not they materially affect the activity or action of the listed elements. Any of the elements
25 or combinations of elements that are recited in this specification in open-ended language (e.g., comprise and derivatives thereof), are considered to additionally be recited in closed-ended language (e.g., consist and derivatives thereof) and in partially closed-ended language (e.g., consist essentially, and derivatives thereof).

The words “preferred” and “preferably” refer to embodiments of the disclosure that
30 may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the disclosure.

In this application, terms such as “a,” “an,” and “the” are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terms “a,” “an,” and “the” are used interchangeably with the term “at least one.” The phrases “at least one of” and “comprises at least one of” followed by a list refers to
5 any of the items in the list and any combination of two or more items in the list.

As used herein, the term “or” is generally employed in its usual sense including “and/or” unless the content clearly dictates otherwise. The term “and/or” means one or all of the listed elements or a combination of any two or more of the listed elements.

Also herein, all numbers are assumed to be modified by the term “about” and in
10 certain embodiments, preferably, by the term “exactly.” As used herein in connection with a measured quantity, the term “about” refers to that variation in the measured quantity as would be expected by the skilled artisan making the measurement and exercising a level of care commensurate with the objective of the measurement and the precision of the measuring equipment used. Herein, “up to” a number (e.g., up to 50) includes the number (e.g., 50).

Also herein, the recitations of numerical ranges by endpoints include all numbers
15 subsumed within that range as well as the endpoints (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.) and any sub-ranges (e.g., 1 to 5 includes 1 to 4, 1 to 3, 2 to 4, etc.).

As used herein, the term “room temperature” refers to a temperature of 20°C to 25°C.

The term “in the range” or “within a range” (and similar statements) includes the
20 endpoints of the stated range.

Reference throughout this specification to “one embodiment,” “an embodiment,”
“certain embodiments,” or “some embodiments,” etc., means that a particular feature,
configuration, composition, or characteristic described in connection with the embodiment is
included in at least one embodiment of the disclosure. Thus, the appearances of such phrases
25 in various places throughout this specification are not necessarily referring to the same
embodiment of the disclosure. Furthermore, the particular embodiments, including features,
configurations, compositions, or characteristics may be combined in any suitable manner in
one or more embodiments.

The above summary of the present disclosure is not intended to describe each
30 disclosed embodiment or every implementation of the present disclosure. The description and
drawings that follow more particularly exemplify illustrative embodiments. In several places
throughout the application, guidance is provided through lists of examples, which examples
may be used in various combinations. In each instance, the recited list serves only as a
representative group and should not be interpreted as an exclusive list. Thus, the scope of the

present disclosure should not be limited to the specific illustrative structures described herein, but rather extends at least to the structures described by the language of the embodiments, and the equivalents of those structures. Any of the elements that are positively recited in this specification as alternatives may be explicitly included in the embodiments or excluded from the embodiments, in any combination as desired. Although various theories and possible mechanisms may have been discussed herein, in no event should such discussions serve to limit the claimable subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic of an exemplary liquid jet application system.

Fig. 2 is a schematic of an exemplary aerosol jet application system using the venturi effect.

Fig. 3 is a schematic of an exemplary aerosol jet application system using ultrasonic energy.

Fig. 4 is a schematic of an exemplary nozzle used in an aerosol jet application system.

Fig. 5 provides schematics of representative examples of assemblies that include multilayer coatings in the rigid metal packaging industry.

Fig. 6 is a schematic of a patterned coating on a food or beverage can end.

Fig. 7 is a schematic of a patterned coating on a lug cap.

Fig. 8 is a schematic of an indexed variable thickness coating.

Fig. 9 is a block diagram of a liquid/aerosol jet coating application process in-line with fabrication.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

The present disclosure provides liquid jet or aerosol jet coating compositions (i.e., coating compositions), particularly metal packaging liquid jet or aerosol jet coating compositions, coated metal substrates, methods – e.g., method of making a metal packaging liquid jet or aerosol jet coating composition, method of coating a metal substrate, and method of making metal packaging (e.g., a container, a portion thereof, or a metal closure) – as well as the metal packaging. Examples of metal packaging containers include food, beverage, aerosol, and general metal packaging containers. Examples of metal closures include twist-off caps or lids with threads or lugs and crowns that are crimped on bottles. Such closures are metal but useful on metal or non-metal packaging containers. Metal packaging also includes pull tabs for an easy open can ends.

The metal packaging liquid jet or aerosol jet coating compositions are particularly useful on food-contact surfaces of such metal packaging containers and metal closures, but may also be used on exterior surfaces of such metal packaging containers and metal closures. Although the metal packaging liquid jet or aerosol jet coating compositions of the present disclosure are particularly useful on a food-contact surface of a metal substrate, they may also be useful on other types of substrates for packaging foods, beverages, or other products such as glass (e.g., glass bottles), rigid and flexible plastic, foil, paper, paperboard, or substrates that are a combination thereof.

The resultant coated food-contact surfaces of metal packaging containers and metal closures of the present disclosure are particularly desirable for packaging liquid-containing products. Packaged products that are at least partially liquid in nature (e.g., wet) place a substantial burden on coatings due to intimate chemical contact with the coatings. Such intimate contact can last for months, or even years. Furthermore, the coatings may be required to resist pasteurization or cooking processes during packaging of the product. In the food or beverage packaging realm, examples of such liquid-containing products include beer, alcoholic ciders, alcoholic mixers, wine, soft drinks, energy drinks, water, water drinks, coffee drinks, tea drinks, juices, meat-based products (e.g., sausages, meat pastes, meat in sauces, fish, mussels, clams, etc.), milk-based products, fruit-based products, vegetable-based products, soups, mustards, pickled products, sauerkraut, mayonnaise, salad dressings, and cooking sauces.

Many coatings that are used to package dry products do not possess the stringent balance of coating properties necessary for use with the above “wet” products. For example, it would not be expected that a coating used on the interior of a decorative metal tin for individually packaged cookies would exhibit the necessary properties for use as an interior soup can coating.

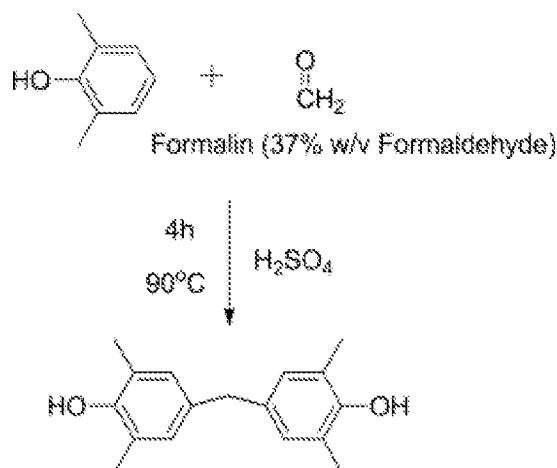
Although containers of the present disclosure may be used to package dry powdered products that tend to be less aggressive in nature towards packaging coatings (e.g., powdered milk, powdered baby formula, powdered creamer, powdered coffee, powdered cleaning products, powdered medicament, etc.), due to the higher volumes in the marketplace, more typically the coatings will be used in conjunction with more aggressive products that are at least somewhat “wet” in nature. Accordingly, packaging coatings formed from liquid or aerosol coating compositions of the present disclosure are preferably capable of prolonged and intimate contact, including under harsh environmental conditions, with packaged products having one or more challenging chemical features, while protecting the underlying

metal substrate from corrosion and avoiding unsuitable degradation of the packaged product (e.g., unsightly color changes or the introduction of odors or off flavors). Examples of such challenging chemical features include water, acidity, fats, salts, strong solvents (e.g., in cleaning products, fuel stabilizers, or certain paint products), aggressive propellants (e.g., aerosol propellants such as certain dimethyl-ether-containing propellants), staining characteristics (e.g., tomatoes), or combinations thereof.

Accordingly, preferably, the metal packaging liquid jet or aerosol jet coating compositions, and preferably, the hardened coatings, of the present disclosure are substantially free of each of bisphenol A, bisphenol F, and bisphenol S; the liquid jet or aerosol jet coating compositions, and preferably, the hardened coatings, of the present disclosure are essentially free of each of bisphenol A, bisphenol F, and bisphenol S; the liquid jet or aerosol jet coating compositions, and preferably, the hardened coatings, of the present disclosure are essentially completely free of each of bisphenol A, bisphenol F, and bisphenol S; or the liquid jet or aerosol jet coating compositions, and preferably, the hardened coatings, of the present disclosure are completely free of each of bisphenol A, bisphenol F, and bisphenol S.

More preferably, the metal packaging liquid jet or aerosol jet coating compositions, and preferably the hardened coatings, of the present disclosure are substantially free of all bisphenol compounds; the liquid jet or aerosol jet coating compositions, and preferably the hardened coatings, of the present disclosure are essentially free of all bisphenol compounds; the liquid jet or aerosol jet coating compositions, and preferably the hardened coatings, of the present disclosure are essentially completely free of all bisphenol compounds; or the liquid jet or aerosol jet coating compositions, and preferably the hardened coatings, of the present disclosure are completely free of all bisphenol compounds.

Preferably, tetramethyl bisphenol F (TMBPF) is not excluded from the liquid jet or aerosol jet coating compositions or hardened coatings of the present disclosure. TMBPF is 4-[(4-hydroxy-3,5-dimethylphenyl)methyl]-2,6-dimethylphenol, shown below, made by the following reaction:



For example, a liquid jet or aerosol jet coating composition is not substantially free of bisphenol A that includes 600 ppm of bisphenol A and 600 ppm of the diglycidyl ether of bisphenol A (BADGE) – regardless of whether the bisphenol A and BADGE are present in the composition in reacted or unreacted forms, or a combination thereof.

The amount of bisphenol compounds (e.g., bisphenol A, bisphenol F, and bisphenol S) can be determined based on starting ingredients; a test method is not necessary and parts per million (ppm) can be used in place of weight percentages for convenience in view of the small amounts of these compounds.

Although, with the notable exception of TMBPF, the intentional addition of many bisphenol compounds is now generally undesirable due to shifting consumer perceptions, it should be understood that non-intentional, trace amounts of bisphenols, may potentially be present in compositions or coatings of the present disclosure due to, e.g., environmental contamination.

Although the balance of scientific evidence available to date indicates that the small trace amounts of bisphenol compounds, such as bisphenol A, that might be released from existing coatings does not pose any health risks to humans, these compounds are nevertheless perceived by some people as being potentially harmful to human health. Consequently, there is a desire by some to eliminate these compounds from coatings on food-contact surfaces.

Also, it is desirable to avoid the use of components that are unsuitable for such surfaces due to factors such as taste, toxicity, or other government regulatory requirements.

For example, in preferred embodiments where the coating constitutes a food-contact surface, the liquid jet or aerosol jet coating composition is “PVC-free.” That is, the liquid jet or aerosol jet coating composition preferably contains, if any, less than 2% by weight of vinyl chloride materials and other halogenated vinyl materials, more preferably less than 0.5% by weight of vinyl chloride materials and other halogenated vinyl materials, and even more

preferably less than 1 ppm of vinyl chloride materials and other halogenated vinyl materials, if any.

As a general guide to minimize potential, e.g., taste and toxicity concerns, a hardened coating formed from the liquid jet or aerosol jet coating composition preferably includes, if it includes any detectable amount, less than 50 ppm, less than 25 ppm, less than 10 ppm, or less than 1 ppm, extractables, when tested pursuant to the Global Extraction Test described in the Test Methods. An example of these testing conditions is exposure of the hardened coating to 10 wt-% ethanol solution for two hours at 121°C, followed by exposure for 10 days in the solution at 40°C.

Such reduced global extraction values may be obtained by limiting the amount of mobile or potentially mobile species in the hardened coating. In this context, “mobile” refers to material that may be extracted from a cured coating according to the Global Extraction Test of the Test Methods. This can be accomplished, for example, by using pure, rather than impure reactants, avoiding the use of hydrolyzable components or bonds, avoiding or limiting the use of low molecular weight additives that may not efficiently react into the coating, and using optimized cure conditions optionally in combination with one or more cure additives. This makes the hardened coatings formed from the liquid jet or aerosol jet coating compositions described herein particularly desirable for use on food-contact surfaces.

Liquid Jet or Aerosol Jet Coating Compositions

According to the present disclosure, a metal packaging (e.g., a food, beverage, or aerosol can or cup) liquid jet or aerosol jet coating composition is provided. Such a coating composition refers to a composition that includes polymer particles in a water-based carrier, thereby forming a water-based polymer dispersion. Herein, a “liquid jet or aerosol jet coating composition” is used interchangeably with “liquid or aerosol jet coating composition,” “liquid or aerosol coating composition,” “coating composition,” and “water-based polymer dispersion.”

Such compositions can form a hardened adherent coating on a substrate, such as a metal substrate. In particular, such compositions may also be useful for coating food, beverage, or aerosol cans, general metal packaging cans or other containers, portions thereof, or metal closures for metal packaging containers or other containers (e.g., closures for glass jars).

Water-Based Polymer Dispersions

A water-based dispersion that forms a “liquid or aerosol jet coating composition” includes polymer particles in a water-based carrier. The water-based carrier includes water as the main (i.e., major) liquid carrier. By this it is meant that the liquid carrier includes at least 51 wt-% water. Although, preferably, no organic solvents or other organic liquids are included in the liquid carrier, in certain embodiments less than 50 wt-% (e.g., ≤ 49 wt-%) of the liquid carrier is an organic liquid. Preferably, less than 25 wt-%, more preferably less than 10 wt-%, and even more preferably less than 1 wt-%, of the liquid carrier includes an organic solvent (e.g., an organic solvent such as ethanol).

The liquid or aerosol jet coating composition is preferably storage stable for at least 2 months, at least 3 months, at least 4 months, at least 5 months, or at least 6 months, at ambient temperature without any phase separation as determined by the unaided human eye.

The solids content of the coating composition is preferably at least 10 wt-%, at least 15 wt-%, or at least 20 wt-%, based on the total weight of the coating composition (prior to incorporating into a liquid jet or aerosol jet coating system).

The solids content of the coating composition is preferably up to 50 wt-%, up to 40 wt-%, or up to 30 wt-%, based on the total weight of the coating composition (prior to incorporating into a liquid jet or aerosol jet coating system).

The amount of polymer particles in the water-based carrier (i.e., concentration of polymer particles in the coating composition) is preferably at least 30 wt-%, at least 50 wt-%, or at least 70 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the cured coating).

The amount of polymer particles in the water-based carrier (i.e., concentration of polymer particles in the coating composition) is preferably up to 99 wt-%, up to 97 wt-%, or up to 95 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the cured coating).

The preferred viscosity range of the liquid jet or aerosol jet coating composition (i.e., water-based dispersion before being subjected to a liquid or aerosol jetting process) may vary for liquid jet application versus aerosol jet application. Viscosity can be measured via a Brookfield viscometer in accordance with ASTM 2196 (2020), Method A. Unless otherwise specified, the viscosity of samples intended for liquid jetting should be measured at 120°F (49°C) and the samples for aerosol jetting should be measured at 80°F (27°C).

The viscosity of the coating composition for a liquid jet application process is preferably at least 1 centipoise (cps), at least 10 cps, or at least 20 cps. The viscosity of the

coating composition for a liquid jet application process is preferably up to 50 centipoise (cps), up to 40 cps, or up to 30 cps.

The viscosity of the coating composition for an aerosol jet application process is preferably at least 1 centipoise (cps), at least 50 cps, or at least 100 cps. The viscosity of the coating composition for an aerosol jet application process is preferably up to 1,000 centipoise (cps), up to 500 cps, or up to 200 cps.

The preferred surface tension range of the liquid jet or aerosol jet coating composition (i.e., water-based dispersion before being subjected to a liquid or aerosol jetting process) may vary for liquid jet application versus aerosol jet application. Surface tension can be measured in accordance with ASTM D1331 (2020), Method C. Unless otherwise specified, the surface tension of samples intended for liquid jetting or aerosol jetting should be measured at 77°F (25°C).

The surface tension of the coating composition for a liquid jet application process is preferably at least 10 milliNewtons per meter (mN/m), at least 20 mN/m, or at least 30 mN/m.

The surface tension of the coating composition for a liquid jet application process is preferably up to 50 mN/m, up to 45 mN/m, or up to 40 mN/m.

The surface tension of the coating composition for an aerosol jet application process is preferably at least 10 milliNewtons per meter (mN/m), at least 20 mN/m, or at least 30 mN/m. The surface tension of the coating composition for an aerosol jet application process is preferably up to 50 mN/m, up to 45 mN/m, or up to 40 mN/m.

The molecular weight of the polymer in the polymer particles in the liquid jet or aerosol jet coating composition may be described by a few key metrics given that a typical polymer covers a range of molecular weights. Number average molecular weight (M_n) is determined by dividing the total weight of a sample by the total number of molecules in that sample. Weight average molecular weight (M_w) is determined by calculating the sum of each distinct molecular weight in the sample multiplied by the weight fraction of the sample at that molecular weight. Polydispersity index (M_w/M_n) is used to express how broad the molecular weight range is of the sample. The higher the polydispersity index, the broader the molecular weight range. The M_n , M_w , and M_w/M_n can all be determined by Gel Permeation Chromatography (GPC), measured against a set of polystyrene standards of varying molecular weights.

The M_n of the polymer particles of the water-based dispersions is at least 2,000 Daltons, preferably at least 3,000 Daltons, and more preferably at least 4,000 Daltons. The M_n of the polymer particles of the water-based dispersions may be in the millions (e.g.,

10,000,000 Daltons), such as can occur with emulsion polymerized acrylic polymers or certain other emulsion polymerized latex polymers, although the Mn may be up to 60,000 Daltons, or up to 40,000 Daltons, or up to 20,000 Daltons. In certain embodiments, the Mn of the polymer particles of the water-based dispersions may be at least 2,000 Daltons and up to 60,000 Daltons, or at least 3,000 Daltons and up to 40,000 Daltons, or at least 4,000 Daltons and up to 20,000 Daltons.

The polymer particles of the water-based dispersions may be made from a polymer having a polydispersity index of less than 4, less than 3, less than 2, or less than 1.5. It may be advantageous, however, for the polymer to have a polydispersity index outside the preceding ranges. For example, without intending to be bound by theory, it may be desirable to have a higher polydispersity index to achieve the benefits of both higher molecular weight (e.g., for flexibility and other mechanic properties) and lower molecular weight (e.g., for flow and leveling) in the same material.

The polymer particles of the water-based dispersion preferably have a particle size distribution with a D50 (preferably, a D90, D95, or a D99) of less than 10 microns, less than 5 microns, or less than 0.5 micron. The polymer particles of the water-based dispersion preferably have a particle size distribution with a D50 (preferably, a D90, D95, or a D99) of at least 0.01 micron, at least 0.05 micron, or at least 0.1 micron. While the most preferred D50 range (less than 0.5 micron) offers the best balance of dispersion stability and jettability, larger D50 samples (0.5 micron or more, or 5 microns or more, or even 10 microns or more), which may exhibit some settling, can still be used if the dispersion is stirred prior to and/or during jetting.

In this context, the “D-values” – D50, D90, D95, and D99 – are the particle sizes which divide a sample’s volume into a specified percentage when the particles are arranged on an ascending particle size basis. For example, for particle size distributions the median is called the D50 (or x50 when following certain ISO guidelines). The D50 is the particle size in microns that splits the distribution with half above and half below this diameter. The Dv50 (or Dv0.5) is the median for a volume distribution. The D90 describes the particle size where ninety percent of the distribution has a smaller particle size and ten percent has a larger particle size. The D95 describes the particle size where ninety five percent of the distribution has a smaller particle size and five percent has a larger particle size. The D99 describes the particle size where ninety nine percent of the distribution has a smaller particle size and one percent has a larger particle size. Unless specified otherwise

herein, D50, D90, D95, and D99 refer to D_v50, D_v90, D_v95, and D_v99, respectively. The D-values specified herein may be determined by laser diffraction particle size analysis.

A useful method for determining particle sizes of the polymer particles in the water-based dispersions and other starting materials (e.g., lubricants, etc.) is laser diffraction particle size analysis. An exemplary device for such analysis is a Beckman Coulter LS 230 Laser Diffraction Particle Size Analyzer or equivalent, calibrated as recommended by the manufacturer. It is believed that the particle size analysis of this analyzer embodies the principles of International Standard ISO 13320:2009(E).

Samples for laser diffraction particle size analysis can be prepared, for example, by diluting the samples in a substantially non-swelling solvent (such as cyclohexanone or 2-butoxyethanol) and shaking them until evenly dispersed. The choice of a suitable solvent will depend upon the particular particles to be tested. Solvent screening tests may need to be conducted to identify a suitable substantially non-swelling solvent. By way of example, a solvent in which a polymer particle swells by about 1% or less (as determined by laser diffraction particle size analysis) would be considered a substantially non-swelling solvent.

The polymer particles may include any suitable combination of one or more thermoplastic polymers, one or more thermoset polymers, or a combination thereof. For certain preferred applications, the polymer particles may include any suitable combination of one or more thermoplastic polymers. The term “thermoplastic” refers to a material that melts and changes shape when sufficiently heated and hardens when sufficiently cooled. Such materials are typically capable of undergoing repeated melting and hardening without exhibiting appreciable chemical change. In contrast, a “thermoset” refers to a material that is crosslinked and does not “melt.”

The polymer material preferably has a melt flow index greater than 15 grams/10 minutes, greater than 50 grams/10 minutes, or greater than 100 grams/10 minutes. The polymer material preferably has a melt flow index of up to 200 grams/10 minutes, or up to 150 grams/10 minutes. The “melt flow index” referred to herein is measured pursuant to ASTM D1238-13 (2013) at 190°C and with a 2.16-kilogram weight.

In certain embodiments, the polymer particles are made from semi-crystalline, crystalline polymers, amorphous polymers, or combinations thereof. Suitable semi-crystalline or crystalline polymers may exhibit any suitable percent crystallinity. In some embodiments, the liquid or aerosol coating composition of the disclosure includes at least one semi-crystalline or crystalline polymer having a percent crystallinity (on a weight basis) of at least 5%, at least 10%, or at least 20%. By way of example, the percent crystallinity for a

given polymer may be assessed via differential scanning calorimetry (DSC) testing using the following equation:

$$\text{Percent crystallinity (\%)} = [A/B] \times 100$$

wherein: “A” is the heat of fusion of the given polymer (i.e., the total area “under” the melting portion of the DSC curve) in Joules per gram (J/g); and
“B” is the heat of fusion in J/g for the 100% crystalline state of the polymer.

For many polymers, a theoretical B value may be available in the scientific literature and such value may be used. For polyester polymers, for example, if such a B value is not available in the literature, then a B value of 145 J/g may be used as an approximation, which is the heat of fusion for 100% crystalline polybutylene terephthalate (PBT) as reported in: Cheng, Stephen; Pan, Robert; and Wunderlich, Bernard; “Thermal analysis of poly(butylene terephthalate) for heat capacity, rigid-amorphous content, and transition behavior,” *Macromolecular Chemistry and Physics*, Volume 189, Issue 10 (1988): 2443-2458.

Preferably, at least one polymer material of the polymer particles (and more preferably substantially all, or all, of the polymer material present in the polymer particles) is at least semi-crystalline (e.g., semi-crystalline or crystalline). The polymer particles may include amorphous polymer material or a blend of at least semi-crystalline polymer material and amorphous polymer material. ASTM-D3418-15 (2015) is an example of a useful methodology for assessing the crystallization properties (crystallization peak temperature) of polymers.

The polymers used may exhibit any suitable glass transition temperature (T_g) or combinations of T_g's. The polymer particles are preferably made from a polymer having a glass transition temperature (T_g) of at least 15°C, at least 20°C, or at least 25°C and a T_g of up to 150°C, up to 125°C, up to 110°C, up to 100°C, up to 80°C, or up to 50°C.

In some embodiments, lower T_g polymers (e.g., having a T_g lower than 15°C, such as those with a T_g of at least 0°C) may be used in making the polymer particles used herein as long as the particles include at least one polymer with a higher T_g (e.g., at least 15°C).

The polymer particles may additionally be of a core-shell morphology (i.e., the outer portion, or shell, of the polymer particle is of a different composition than the inner portion, or core). In such cases, the shell ideally comprises 10% by weight or greater of the total polymer particles, and the T_g preferences above would only apply to the shell of the polymer particle. In other words, the shell of the polymer particle is preferably made from a polymer

having a Tg of at least 15°C, at least 20°C, or at least 25°C and a Tg of up to 150°C, up to 125°C, up to 110°C, up to 100°C, up to 80°C, or up to 50°C.

In embodiments incorporating a crystalline or semi-crystalline polymer, the polymer particles are preferably made from a crystalline or semi-crystalline polymer having a melting point of at least 40°C, and a melting point of up to 300°C.

In preferred embodiments, substantially all (i.e., more than 50 wt-%) of the polymer material of the polymer particles exhibits such a melting point or Tg. Classic amorphous polymers do not, for example, exhibit any discernible melting point (e.g., do not exhibit a DSC melting peak) nor include any crystalline regions. Thus, such classic amorphous polymers would be expected to exhibit a percent crystallinity of 0%. Accordingly, liquid jet and aerosol jet coating compositions of the disclosure may include one or more amorphous polymers having a percent crystallinity of 0% or substantially 0%. If desired, however, liquid jet and aerosol jet coating compositions of the disclosure may include one or more “amorphous” polymers having a percent crystallinity other than 0 (e.g., less than 5%, less than 2%, less than 1%, less than 0.5%, less than 0.1%, etc.).

The one or more polymers of the polymer particles may be aliphatic or aromatic, or a combination of one or more aliphatic polymers and one or more aromatic polymers. Similarly, the one or more polymer may be saturated or unsaturated, or a combination of one or more saturated polymers and one or more unsaturated polymers.

Suitable polymer particles can be prepared from water (e.g., latex polymers) or from organic solvents (e.g., nonane, decane, dodecane, or isohexadecane), or combinations thereof. Water-based polymers are preferred because of cost considerations, to keep VOC levels down during processing, and to keep residual organic solvents out of the liquid or aerosol coating compositions.

The polymer particles may be emulsion, suspension, solution, or dispersion polymerized polymer particles (i.e., particles made from an emulsion, suspension, solution, or dispersion polymerization process). Typically, water-dispersible polymers include self-emulsifiable groups (e.g., carboxylic, sulphonic, phosphonic acid groups, or salts thereof), although this is not a requirement. Neutralizing agents (e.g., amines, ammonia, or ammonium hydroxide), particularly volatile ones, can also be used in making such polymer particles, as is well-known to those skilled in the art. Conversely, if desired, base groups that are neutralized with acids may also be used. Non-ionic polar groups may also alternatively or additionally be used. In embodiments in which acid groups are used to stabilize the polymer particle dispersions, the overall polymer particle may have any suitable acid number so long

as the polymer particle is preferably capable of being stably dispersed into water. While not intending to be bound by any theory, it is believed that the presence of at least some acid groups in the polymer particle is desirable, for example, to enhance the liquid stability of the polymer particle dispersion. For examples that use acid-functional self-emulsifiable groups, the total polymer particle has a preferred acid number of at least 5, at least 20, or at least 30 milligrams of KOH per gram of polymer, and a preferred acid number of up to 100, up to 130, or up to 180 milligrams of KOH per gram of polymer. The acid number of the polymer particles can be measured in accordance with BS EN ISO 3682-1998 standard.

The polymer of the polymer particles may be a polyacrylic (i.e., acrylic or acrylate or polyacrylate) (e.g., a solution-polymerized acrylic polymer, an emulsion polymerized acrylic polymer, or combination thereof), polyether, polyolefin, polyester, polyurethane, polycarbonate, polystyrene, or a combination thereof (i.e., copolymer or mixture thereof such as polyether-acrylate copolymer). The polymers may be engineering plastics. Engineering plastics are a group of thermoplastic materials that have better mechanical and/or thermal properties than the more widely used commodity plastics (such as polystyrene, polypropylene, and polyethylene). Examples of engineering plastics include acrylonitrile butadiene styrene (ABS), polycarbonates, and polyamides. Preferably, the polymer of the polymer particles is a polyacrylic (e.g., an acid- or anhydride-functional organic-solution polymerized acrylic polymer, an emulsion polymerized acrylic polymer, or a combination thereof), a polyether, a polyolefin, a polyester, or a combination thereof (e.g., a polyether-acrylate copolymer, a polyester-acrylate copolymer, and the like).

Individual particles may be made of one polymer or two or more polymers. Individual particles may be uniform throughout or have a “core-shell” configuration having 1, 2, 3, or more “shell” layers or have a gradient architecture (e.g., a continuously varying architecture). Such “core-shell” particles may include, for example, multi-stage latexes created via the emulsion polymerization of two or more different stages, emulsion polymerizations conducted using a polymeric surfactant, or combinations thereof. Populations of particles may include mixtures of polymers, including mixtures of uniform and core-shell particles.

In preferred embodiments, the inclusion of a sufficient number of cyclic groups, and preferably aryl and/or heteroaryl groups (e.g., phenylene groups), in the polymers is an important factor for achieving suitable coating performance for food-contact packaging coatings, especially when the product to be packaged is a so called “hard-to-hold” food or beverage product. Sauerkraut is an example of a hard-to-hold product. Although cyclic

groups providing such performance are often aryl or heteroaryl groups, suitable aliphatic cyclic groups such as, e.g., aliphatic bridged bicyclic (e.g., norbornane or norbornene groups), aliphatic bridged tricyclic groups (e.g., tricyclodecane groups), cyclobutane groups (e.g., as provided using structural units derived from 2,2,4,4-tetramethyl-1,3-

5 cyclobutanediol), cyclobutene groups, or spirobicyclic groups (e.g., as provided using 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (PSG)) may provide such performance.

For example, when the polymer particles are formed from certain polyether or polyester polymers, cyclic groups, and more preferably aryl and/or heteroaryl groups, 10 preferably constitute at least 25 wt-%, more preferably at least 30 wt-%, even more preferably at least 35 wt-%, and optimally at least 45 wt-% of such polymers. The upper concentration of cyclic groups (e.g., aryl/heteroaryl groups) is not particularly limited, but preferably the amount of such groups is configured such that the T_g of the polymer is preferably within the T_g ranges discussed herein. The total amount of cyclic groups (e.g., 15 aryl and/or heteroaryl groups) in such polymers will typically constitute less than about 80 wt-%, more preferably less than 75 wt-%, even more preferably less than about 70 wt-%, and optimally less than 60 wt-% of the polyether polymer. The total amount of cyclic groups (e.g., aryl and/or heteroaryl groups) in such polymers can be determined based on the weight of cyclic group-containing polymerizable compound (e.g., aryl- or heteroaryl-containing 20 polymerizable compound) incorporated into the polymers and the weight fraction of such polymerizable compound that constitutes cyclic groups (e.g., aryl or heteroaryl groups).

Preferred aryl or heteroaryl groups include less than 20 carbon atoms, more preferably less than 11 carbon atoms, and even more preferably less than 8 carbon atoms. The aryl or heteroaryl groups preferably have at least 4 carbon atoms (e.g., a furanylene group), more 25 preferably at least 5 carbon atoms, and even more preferably at least 6 carbon atoms. Substituted or unsubstituted phenylene groups are preferred aryl or heteroaryl groups.

Alternatively, at least some, or even all, of the cyclic groups are polycyclic groups (e.g., bicyclic, tricyclic, or polycyclic groups having 4 or more rings).

The polymer particles may include a polyester polymer. Suitable polyesters include 30 polyesters formed from one or more suitable polycarboxylic acid components (e.g., dicarboxylic acid components, tricarboxylic acid components, tetracarboxylic acid components, etc.) and one or more suitable polyol components (e.g., diol components, triol components, polyols having four hydroxyl groups, etc.). One or more other comonomers

may optionally be used, if desired. Dicarboxylic acid components and diol components are preferred.

Suitable dicarboxylic acid components include, for example, aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phthalic acid, naphthalenedicarboxylic acid (e.g., 2,6-naphthalene dicarboxylic acid), and furandicarboxylic acid (e.g., 2,5-furandicarboxylic acid); aliphatic dicarboxylic acids such as adipic acid, cyclohexane dicarboxylic acid, sebacic acid and azelaic acid; unsaturated acids such as maleic anhydride, itaconic acid, and fumaric acid; and mixtures thereof. Examples of other suitable polycarboxylic acids (or anhydrides) include benzene-pentacarboxylic acid; mellitic acid; 1,3,5,7 naphthalene-tetracarboxylic acid; 2,4,6 pyridine-tricarboxylic acid; pyromellitic acid; trimellitic acid; trimesic acid; 3,5,3',5'-biphenyltetracarboxylic acid; 3,5,3',5'-bipyridyltetracarboxylic acid; 3,5,3',5'-benzophenonetetracarboxylic acid; 1,3,6,8-acridinetetracarboxylic acid; 1,2,4,5-benzenetetracarboxylic acid; nadic anhydride; trimellitic anhydride; pyromellitic anhydride, and mixtures thereof. Anhydrides or esters of the
15 aforementioned acids and mixtures of such acids, anhydrides or esters may also be used.

Suitable diol components include, for example, polymethylene glycols represented by the formula $\text{HO}-(\text{CH}_2)_n\text{-OH}$ (where n is about 2 to 10) such as ethylene glycol, propylene glycol, butanediol, hexanediol and decamethylene glycol; branched glycols represented by the formula $\text{HO-CH}_2\text{-C(R}_2\text{)-CH}_2\text{-OH}$ (where R is an alkyl group having 1 to 4 carbon atoms) such as neopentyl glycol; diethylene glycol and triethylene glycol; diols having a cyclohexane ring such as cyclohexane dimethanol (CHDM); 2-methyl-1,3 propane diol; diols having a cyclobutane ring such as 2,2,4,4-tetramethyl-1,3-cyclobutanediol; isosorbide; tricyclodecanedimethanol; spirobicyclic diols (e.g., 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (PSG)); and mixtures thereof. Glycerol, trimethylol
20 propane (TMP), and other suitable trifunctional or higher polyols may also be used alone or in combination with any other suitable polyol.

The polyester polymer particles are preferably made from semi-crystalline or crystalline polymers. Suitable exemplary crystalline and semi-crystalline polyester polymers include polyethylene terephthalate ("PET"), copolymers of PET such as PET/I, polybutylene terephthalate ("PBT"), polyethylene naphthalate ("PEN"), poly-1,4-cyclohexylenedimethylene terephthalate, and copolymers and combinations thereof. The polyester material may be formed from ingredients including dimer fatty acids. Non-limiting examples of useful commercially available polyester materials may include polyesters commercially available under the tradename DYNAPOL such as, for example, DYNAPOL
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L912 (includes polycyclic groups derived from tricyclodecanedimethanol), DYNAPOL L952, DYNAPOL P1500, DYNAPOL P1500 HV (has a melting point temperature of about 170°C, a glass transition temperature of about 20°C, and a number average molecular weight of approximately 20,000), DYNAPOL P1510, and DYNAPOL P1550 (each available from
5 Hiils AG and based on monomers including terephthalic acid and/or isophthalic acid); polyester materials commercially available under the TRITAN tradename (available from Eastman Chemical Company and based on monomers including 2,2,4,4-Tetramethyl-1,3-cyclobutanediol); and polyester materials commercially available under the tradename GRILTEX such as, for example, GRILTEX DD2267EG and GRILTEX D2310EG (each
10 available from EMS-Chemie and based on monomers including terephthalic acid and/or isophthalic acid).

Exemplary polyester polymers that may be used in making suitable polymer particles are described, for example, in U.S. Pat. Pub. No. 2014/0319133 (Castelberg et al.), U.S. Pat. Pub. No. 2015/0344732 (Witt-Sanson et al.), U.S. Pat. Pub. No. 2016/0160075 (Seneker et
15 al.), International Application No. PCT/US2018/051726 (Andriot et al.), U.S. Pat. No. 5,464,884 (Nield et al.), U.S. Pat. No. 6,893,678 (Hirose et al.), U.S. 7,198,849 (Stapperfenne et al.), U.S. Pat. No. 7,803,415 (Kiefer-Liptak et al.), U.S. Pat. No. 7,981,515 (Ambrose et al.), U.S. Pat. No. 8,133,557 (Parekh et al.), U.S. Pat. No. 8,367,171 (Stenson et al.), U.S. 8,574,672 (Doreau et al.), U.S. Pat. No. 9,096,772 (Lespinasse et al.), U.S. Pat. No. 9,011,999
20 (Cavallin et al.), U.S. Pat. No. 9,115,241 (Gao et al.), U.S. Pat. No. 9,187,213 (Prouvost et al.), U.S. Pat. No. 9,321,935 (Seneker et al.), U.S. Pat. No. 9,650,176 (Cavallin et al.), U.S. Pat. No. 9,695,264 (Lock et al.), U.S. Pat. No. 9,708,504 (Singer et al.), U.S. Pat. No. 9,920,217 (Skillman et al.), U.S. Pat. No. 10,131,796 (Martinoni et al.), U.S. Pat. Pub. No. 2020/0207516 (Seneker et al.), and WO 2021/105970 (Riazzi et al.).

Polyester polymers having C4 rings may be used such as, for example, are present in certain structural segments derived from cyclobutanediol-type compounds such as, e.g., including 2,2,4,4-tetramethyl-1,3-cyclobutanediol). Exemplary such polyesters including
25 such C4 rings are described, for example, in WO2014/078618 (Knotts et al.), U.S. Pat. No. 8,163,850 (Marsh et al.), U.S. Pat. No. 9,650,539 (Kuo et al.), U.S. Pat. No. 9,598,602 (Kuo et al.), U.S. Pat. No. 9,487,619 (Kuo et al.), U.S. Pat. No. 9,828,522 (Argyropoulos et al.),
30 and U.S. Pat. Pub. No. 2020/0207516 (Seneker et al.).

Preferably, the polymer particles may include a polyether polymer. The polyether polymer may contain a plurality of aromatic segment, more typically aromatic ether segments. The polyether polymer may be formed using any suitable reactants and any

suitable polymerization process. The polyether polymer may be formed, for example, from reactants including an extender compound (e.g., a diol, which is preferably a polyhydric phenol, more preferably a dihydric phenol; a diacid; or a compound having both a phenol hydroxyl group and a carboxylic group) and a polyepoxide. In preferred embodiments, the polyepoxide is a polyepoxide of a polyhydric phenol (more typically a diepoxide of, e.g., a diglycidyl ether of, a dihydric phenol). Preferably, (i) the polyhydric phenol compound is an ortho-substituted diphenol (e.g., tetramethyl bisphenol F), (ii) the diepoxide is a diepoxide of an ortho-substituted diphenol (e.g., tetramethyl bisphenol F), or (iii) both (i) and (ii).

A polyether polymer may be formed from reactants including a diepoxide of an ortho-substituted diphenol (e.g., the diglycidyl ether of tetramethyl bisphenol F) and a dihydric phenol having only one phenol ring (e.g., hydroquinone, resorcinol, catechol, or a substituted variant thereof).

A polyether polymer may be prepared from reactants including a diepoxide (typically a diglycidyl ether or diglycidyl ester) that is not derived from a polyhydric phenol, and which includes one or more backbone or pendant aryl or heteroaryl groups. Such aromatic diepoxides may be prepared, for example, from aromatic compounds having two or more reactive groups such as diols, diacids, diamines, and the like. Suitable such exemplary aromatic compounds for use in forming the aromatic diepoxides include 1-phenyl-1,2-propanediol; 2-phenyl-1,2-propanediol; 1-phenyl-1,3-propanediol; 2-phenyl-1,3-propanediol; 1-phenyl-1,2-ethanediol; vanillyl alcohol; 1,2-, 1,3- or 1,4-benzenedimethanol; furandimethanol (e.g., 2,5-furandimethanol); terephthalic acid; isophthalic acid; and the like.

A polyether polymer may be prepared from reactants including one or more aliphatic polyepoxides, which are typically aliphatic diepoxides, and more typically cycloaliphatic diepoxides. Exemplary aliphatic diepoxides include diepoxides of (which are typically diglycidyl ethers of): cyclobutane diol (e.g., 2,2,4,4-tetramethyl-1,3-cyclobutanediol), isosorbide, cyclohexanedimethanol, neopentyl glycol, 2-methyl 1,3-propanediol, tricyclodecanedimethanol, 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (PSG), and mixtures thereof

Exemplary reactants, polymerization processes, and polyether polymers that may be used in making suitable polymer particles are described in U.S. Pat. No. 7,910,170 (Evans et al.), U.S. Pat. No. 9,409,219 (Niederst et al.), U.S. Pat. Pub. No. 2013/0280455 (Evans et al.), U.S. Pat. Pub. No. 2013/0316109 (Niederst et al.), U.S. Pat. Pub. No. 2013/0206756 (Niederst et al.), U.S. Pat. Pub. No. 2015/0021323 (Niederst et al.), International Pub. Nos. WO 2015/160788 (Valspar Sourcing), WO 2015/164703 (Valspar Sourcing), WO

2015/057932 (Valspar Sourcing), WO 2015/179064 (Valspar Sourcing), WO 2018/125895 (Valspar Sourcing), and WO 2021/105970 (SWIMC LLC).

The polyether polymers may alternatively be formed from ingredients that do not include any bisphenols or any epoxides of bisphenols, although non-intentional, trace amounts may potentially be present due to, e.g., environmental contamination. Examples of suitable reactants for forming such bisphenol-free polyether polymers include any of the diepoxides derived from materials other than bisphenols described in the patent documents referenced in the preceding paragraph and any of the extender compounds other than bisphenols disclosed in such patent documents. Hydroquinone, catechol, resorcinol, and substituted variants thereof, are non-limiting examples of suitable extender compounds for use in making such bisphenol-free polyether polymers.

Preferably, the polymer particles may include a polymer formed via free-radical polymerization of ethylenically unsaturated monomers, with acrylic polymers being preferred examples of such polymers. Such polymers are referred to herein as “acrylic polymers” for convenience given that such polymers typically include one or more monomers selected from (meth)acrylates or (meth)acrylic acid. Preferred acrylic polymers include organic-solution polymerized acrylic polymers and emulsion polymerized acrylic latex polymers. A suitable acrylic polymer includes a reaction product of components that include a (meth)acrylic acid ester, an optional ethylenically unsaturated mono- or multi-functional acid, and an optional vinyl compound. For example, the acrylate film-forming polymer could be a reaction product of components that include ethyl acrylate and/or butyl acrylate, acrylic acid and/or methacrylic acid, and styrene and/or cyclohexyl methacrylate (preferably in the presence of 2,2'-azobis(2-methyl-butyronitrile) and tert-butyl peroxybenzoate free radical initiators).

Examples of suitable (meth)acrylic acid esters (i.e., methacrylic acid esters and acrylic acid esters) include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, benzyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, lauryl (meth)acrylate, isobornyl (meth)acrylate, octyl (meth)acrylate, and nonyl (meth)acrylate. Any suitable isomer or combination of isomers of the above may be used. By way of example, disclosure of “butyl (meth)acrylate” is intended to disclose all isomers such as n-butyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, and the like. In general, as disclosed

herein, unless specifically indicated to the contrary, disclosure of all isomers for a given monomer is intended.

Examples of suitable ethylenically unsaturated mono- or multi-functional acids include methacrylic acid, acrylic acid, crotonic acid, itaconic acid, maleic acid, mesaconic acid, citraconic acid, sorbic acid, and fumaric acid.

Examples of suitable vinyl compounds include styrene, halostyrene, isoprene, a conjugated butadiene, alpha-methylstyrene, vinyl toluene, vinyl naphthalene, vinyl chloride (which is not preferred), acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate, vinyl cyclohexane, vinyl cyclooctane, vinyl cyclohexene, and vinyl stearate.

Examples of commercially available acrylic polymers include those available under the trade names VIACRYL SC 454/50BSNB, VIACRYL SC383w/50WA, and VANCERYL 2900 DEV (all from Cytec Industries Inc., West Patterson, NJ), as well as NEOCRYL A-639, NEOCRYL XK-64, URACON CR203 M3, and URACON CS113 S1G (all from DSM Neoresins BV, 5140 AC Waalwijk, Netherlands).

Exemplary acrylic polymers that may be used in making suitable polymer particles are described in U.S. Pat. No. 8,168,276 (Cleaver et al.), U. S. Pat. No. 7,189,787 (O'Brien), U.S. Pat. No. 7,592,047 (O'Brien et al.), U.S. Pat. No. 9,181,448 (Li et al.), U.S. Pat. No. 9,394,456 (Rademacher et al.), U.S. Pat. Pub. No 2016/0009941 (Rademacher et al.), U.S. Pat. Pub. No. US2016/0376446 (Gibanel et al.), U.S. Pat. Pub. No. 2017/0002227 (Gibanel et al.), U.S. Pat. Pub. No. 2018/0265729 (Gibanel et al.), WO2016/196174 (Singer et al.), WO2016/196190 (Singer et al.), WO2017/112837 (Gibanel et al.), WO2017/180895 (O'Brien et al.), WO2018/085052 (Gibanel et al.), WO2018/075762 (Gibanel et al.), WO2019/078925 (Gibanel et al.), WO2019/046700 (O'Brien et al.), and WO2019/046750 (O'Brien et al.).

The polymer particles may include dried latex particles that include both polyether polymer and acrylic polymer. Examples of such latex particles are described, e.g., in WO2017/180895 (O'Brien et al.) and International App. No. WO2019046700 (O'Brien et al.).

Preferably, the polymer particles may include a polyolefin polymer. Examples of suitable polyolefin polymers include maleic-modified polyethylene, maleic-modified polypropylene, ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, propylene acrylic acid copolymers, propylene methacrylic acid copolymers, and ethylene vinyl alcohol copolymers.

Examples of commercially available polyolefin polymers include those available under the trade names DOW PRIMACOR 5980i, DUPONT NUCREL, POLYBOND 1103, NIPPON SOARNOL (EVOH), ARKEMA OREVAC 18751, and ARKEMA OREVAC 18360. Exemplary polyolefin polymers that may be used in making suitable polymer particles are described in U.S. Pat. No. 9,000,074 (Choudhery), U.S. Pat. No. 8,791,204 (Choudhery), International Pub. No. WO 2014/140057 (Akzo Nobel), U.S. Pat. No. 8,722,787 (Romick et al.), U.S. Pat. No. 8,779,053 (Lundgard et al.), and U.S. Pat. No. 8,946,329 (Wilbur et al.).

Suitable polyolefin particles may be prepared from aqueous dispersions of polyolefin polymer. See, for example, U.S. Pat. No. 8,193,275 (Moncla et al.) for a description of suitable processes for producing such aqueous polyolefin dispersions. Examples of commercially available aqueous polyolefin dispersions include the CANVERA line of products available from Dow, including, for example, the CANVERA 1110 product, the CANVERA 3110-series, and the CANVERA 3140-series.

The polymer particles may include an unsaturated polymer in combination with one or both of an ether component or a metal drier. The ether component may be present in the unsaturated polymer itself. While not intending to be bound by theory, it is believed that the presence of a suitable amount of unsaturation (e.g., aliphatic or cycloaliphatic carbon-carbon double bonds such as present in, e.g., norbornene groups and unsaturated structural units derived from maleic anhydride, itaconic acid, functionalized polybutadiene, and the like) in combination with a suitable amount of ether component or metal drier (e.g., aluminum, cobalt, copper, oxides thereof, salts thereof) can result in molecular weight build during thermal cure of the liquid jet or aerosol jet coating composition to form a hardened coating. See, for example, U.S. Pat. No. 9,206,332 (Cavallin et al.) for further discussion of such reaction mechanisms and suitable materials and concentrations. The polymer of the polymer particles may have an iodine value of at least 10, at least 20, at least 35, or at least 50. The upper range of suitable iodine values is not particularly limited, but in most such embodiments the iodine value typically will not exceed about 100 or about 120. The aforementioned iodine values are expressed in terms of the centigrams of iodine per gram of the material. Iodine values may be determined, for example, using ASTM D 5768-02 (Reapproved 2006) entitled "Standard Test Method for Determination of Iodine Values of Tall Oil Fatty Acids."

Optional Additives

The liquid jet or aerosol jet coating composition of the present disclosure may include one or more other optional additives to provide desired effects. For example, such optional additives may be included in the coating composition to enhance composition aesthetics, to facilitate manufacturing, processing, handling, and application of the composition, and to further improve a particular functional property of the coating composition or a hardened coating resulting therefrom. One or more optional additives may form a part of the particles themselves.

Because hardened coatings of the present disclosure are preferably used on food-contact surfaces, it is desirable to avoid the use of additives that are unsuitable for such surfaces due to factors such as taste, toxicity, or other government regulatory requirements.

Examples of such optional additives, particularly those suitable for use in coatings used on food-contact surfaces, include lubricants, adhesion promoters, crosslinkers, catalysts, colorants (e.g., pigments or dyes), ferromagnetic particles, degassing agents, levelling agents, wetting agents, matting agents, surfactants, flow control agents, heat stabilizers, anti-corrosion agents, adhesion promoters, inorganic fillers, metal driers, and combinations thereof. The liquid jet or aerosol jet coating composition may include one or more lubricants, pigments, crosslinkers, or a combination thereof.

In preferred embodiments, liquid jet or aerosol jet coating compositions of the present disclosure include one or more lubricants, e.g., for flexibility. In this context, a lubricant is a compound that reduces the friction at the surface of a coating to impart abrasion resistance to the finished coated metal substrate. It is distinct from a flow improver that aids in the flow of the coating composition and application of a coating to a metal substrate.

Examples of suitable lubricants include carnauba wax, synthetic wax (e.g., Fischer-Tropsch wax), polytetrafluoroethylene (PTFE) wax, polyolefin wax (e.g., polyethylene (PE) wax, polypropylene (PP) wax, and high-density polyethylene (HDPE) wax), amide wax (e.g., micronized ethylene-bis-stearamide (EBS) wax), combinations thereof, and modified version thereof (e.g., amide-modified PE wax, PTFE-modified PE wax, and the like). The lubricants may be micronized waxes, which may optionally be spherical. Lubricants facilitate manufacture of metal cans, particularly metal riveted can ends and pull tabs, by imparting lubricity, and thereby flexibility, to sheets of coated metal substrates.

One or more lubricants may be present in a liquid jet or aerosol jet coating composition of the present disclosure in an amount of at least 0.1 wt-%, at least 0.5 wt-%, or at least 1 wt-%, based on the total solids content of the coating composition (i.e., the total

weight of the overall hardened coating). Further, one or more lubricants may be present in an amount of up to 4 wt-%, up to 3 wt-%, or up to 2 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). The concentrations in the hardened coating are equivalent to the concentrations of the starting materials in the liquid jet or aerosol jet coating composition.

The lubricant may be present in the polymer particles, on the polymer particles, in another ingredient used to form the liquid jet or aerosol jet coating composition, or a combination thereof. The lubricant may also be applied in a second liquid jet or aerosol jet coating composition that is applied in a separate layer.

Examples of suitable commercially available lubricants include the CERETAN line of products from Munzing (e.g., the CERETAN MA 7020, MF 5010, MM 8015, MT 9120, and MXD 3920 products); the LUBA-PRINT line of products from Munzing (e.g., the LUBA-PRINT 255/B, 276/A (ND), 351/G, 501/S-100, 749/PM, and CA30 products); the SST-52, S-483, FLUOROSLIP 893-A, TEXTURE 5347W, and SPP-10 products from Shamrock; the CERAFLLOUR line of products from BYK (e.g., the CERAFLLOUR 981, 988, 996, 258, and 970 products); and the CERACOL 607 product from BYK. In some embodiments, PTFE-free lubricants (i.e., those that do not contain polytetrafluoroethylene) are preferred. In some embodiments, the coating composition is free of any lubricants made using fluorine-containing ingredients.

Particle sizes of some of these lubricants, and methods used to determine such particle sizes as identified by the suppliers (although, herein, such lubricant particle sizes may be measured by laser diffraction particle size analysis), are presented in the following table.

Supplier	Lubricant	Chemistry of Lubricant*	Particle Size*	Method*
Munzing	Ceretan MA 7020	Micronized ethylene-bis-stearamide wax	D99 < 20 μm / D50 < 5 μm	LV 5 ISO 13320
Munzing	Ceretan MF 5010	Spherical, micronized PTFE modified polyolefin wax	D99 < 10 μm / D50 < 4 μm	LV 5 ISO 13320
Munzing	Ceretan MM 8015	Spherical, micronized montan wax	D99 < 15 μm / D50 < 6 μm	LV 5 ISO 13320
Munzing	Ceretan MT 9120	High melting, spherical, micronized Fischer-Tropsch wax	D99 < 20 μm / D50 < 7 μm	LV 5 ISO 13320
Munzing	Ceretan MXD 3920	Coated, micronized wax with diamond-like hardness	D99 < 20 μm / D50 < 4 μm	LV 5 ISO 13320
Munzing	LUBA-print 255/B	Carnauba wax dispersion	D50: 2-3 μm / D98: < 6 μm	Picture-Particle-Analyzing System

Munzing	LUBA-print 276/A	Polyethylene-wax / PTFE dispersion	D50: 2-3 μm / D98: < 8 μm	Picture-Particle-Analyzing System
Munzing	LUBA-print 351/G	Functional blend wax dispersion	D50: 2-3 μm / D98: < 5 μm	Picture-Particle-Analyzing System
Munzing	LUBA-print 501/S-100	Polyethylene-wax dispersion	D50: 2.5-4 μm / D98: < 8 μm	Picture-Particle-Analyzing System
Munzing	LUBA-print 749/PM	Amide-wax dispersion	D50: 2-3 μm / D98: < 5 μm	Picture-Particle-Analyzing System
Munzing	LUBA-print CA 30	Carnauba wax dispersion	D98: 3.0 μm	Single pass test
BYK	Ceraflour 981	Micronized PTFE	D50: 3 μm / D90: 6 μm	Laser diffraction - volume distribution
BYK	Ceraflour 988	Micronized, amide-modified polyethylene wax	D50: 6 μm / D90: 13 μm	Laser diffraction - volume distribution
BYK	Ceraflour 996	Micronized, PTFE-modified polyethylene wax	D50: 6 μm / D90: 11 μm	Laser diffraction - volume distribution
BYK	Ceraflour 970	Micronized polypropylene wax	D50: 9 μm / D90: 14 μm	Laser diffraction - volume distribution
BYK	Ceramat 258	Dispersion of an oxidized HDPE wax	30 μm	Hegman
BYK	Ceracol 607	PTFE-modified polyethylene wax dispersion	D50: 4 μm / D90: 10 μm	Laser diffraction - volume distribution

*According to Manufacturer's Literature

In preferred embodiments, liquid jet or aerosol jet coating compositions of the present disclosure include one or more crosslinkers and/or catalysts. Additionally, or alternatively, the liquid jet or aerosol jet coating composition may include one or more self-crosslinkable polymers.

The term "crosslinker" refers to a molecule capable of forming a covalent linkage between polymers or between two different regions of the same polymer. Examples of suitable crosslinkers include carboxyl-reactive curing resins, with beta-hydroxyalkyl-amide crosslinkers being preferred such crosslinkers (e.g., available commercially under the trade name PRIMID from EMS-Griltech (e.g., the PRIMID XL-552 and PRIMID QM-1260 products)) and hydroxyl-curing resins such as, for example, phenolic crosslinkers, blocked isocyanate crosslinkers, and aminoplast crosslinkers. Other suitable curing agents may

include benzoxazine curing agents such as, for example, benzoxazine-based phenolic resins or hydroxy alkyl ureas. Examples of benzoxazine-based curing agents are provided in U.S. Pat. Pub. No. 2016/0297994 (Kuo et al.). Examples of hydroxy alkyl ureas are provided in U.S. Pat. Pub. No. 2017/0204289 (Kurtz et al.). Phenolic crosslinkers include the

5 condensation products of aldehydes with phenols. Formaldehyde and acetaldehyde are preferred aldehydes. Various phenols can be employed such as phenol, cresol, p-phenylphenol, p-tert-butylphenol, p-tert-amylphenol, and cyclopentylphenol.

Aminoplast crosslinkers are typically the condensation products of aldehydes such as formaldehyde, acetaldehyde, crotonaldehyde, and benzaldehyde with amino or amido group-
10 containing substances such as urea, melamine, and benzoguanamine. Examples of suitable aminoplast crosslinking resins include benzoguanamine-formaldehyde resins, melamine-formaldehyde resins, esterified melamine-formaldehyde, and urea-formaldehyde resins. One specific example of a suitable aminoplast crosslinker is the fully alkylated melamine-formaldehyde resin commercially available from Cytac Industries, Inc. under the trade name
15 of CYMEL 303.

Examples of other suitable crosslinkers (e.g., phenolic crosslinker, amino crosslinker, or a combination thereof) and catalysts (e.g., a titanium-containing catalyst, a zirconium-containing catalyst, or a combination thereof) are described in U.S. Pat. No. 8,168,276 (Cleaver et al.).

20 Preferably, the liquid jet or aerosol jet coating composition does not include any added crosslinkers. In such embodiment, the polymer of the particles may, or may not, be a self-crosslinking polymer, depending on the chemistry of the selected polymer and the desired coating properties.

One or more crosslinkers may be present in a liquid jet or aerosol jet coating
25 composition of the present disclosure in an amount of at least 0.1 wt-%, at least 1 wt-%, at least 2 wt-%, at least 5 wt-%, or at least 8 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). One or more crosslinkers may be present in an amount of up to 40 wt-%, up to 30 wt-%, up to 20 wt-%, or up to 10 wt-%, based on the total solids content of the coating composition (i.e., the total
30 weight of the overall hardened coating). The concentrations in the hardened coating are equivalent to the concentrations of the starting materials in the liquid jet or aerosol jet coating composition.

One or more catalysts may be present in a liquid jet or aerosol jet coating composition of the present disclosure in an amount of at least 0.01 wt-%, based on the total weight of the

liquid jet or aerosol jet coating composition, or the total weight of the overall hardened coating. One or more catalysts may be present in an amount of up to 5 wt-%, based on the total weight of the liquid jet or aerosol jet coating composition, or the total weight of the overall hardened coating. The concentrations in the hardened coating are equivalent to the concentrations of the starting materials in the liquid jet or aerosol jet coating composition.

In preferred embodiments, liquid jet or aerosol jet coating compositions of the present disclosure include one or more colorants, such as a pigment and/or dye. Examples of suitable colorants for use in the liquid jet or aerosol jet coating composition include titanium dioxide, barium sulfate, carbon black, and iron oxide, and may also include organic dyes and pigments.

One or more colorants may be present in a liquid jet or aerosol jet coating composition of the present disclosure in an amount of, for example, at least 1 wt-%, at least 2 wt-%, at least 5 wt-%, at least 10 wt-%, or at least 15 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). One or more colorants may be present in an amount of up to 50 wt-%, up to 40 wt-%, up to 30 wt-%, or up to about 20%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). The concentrations in the hardened coating are equivalent to the concentrations of the starting materials in the liquid jet or aerosol jet coating composition. The use of a higher colorant concentration may be advantageous to achieve good coverage with thinner coatings.

Suitable colorants may be either pigments or dyes, but pigments are preferred for food contact (i.e., interior) applications because dyes can have low molecular weight components that could contribute to increased migration into the food or beverage. In addition, pigments used for food contact should meet government regulatory requirements for food contact ingredients, such as FDA 21 CFR § 175.300.

Liquid jet or aerosol jet coating compositions of the present disclosure may include one or more inorganic fillers. Exemplary inorganic fillers used in the liquid jet or aerosol jet coating composition of the present disclosure include, for example, clay, mica, aluminum silicate, fumed silica, magnesium oxide, zinc oxide, barium oxide, calcium sulfate, calcium oxide, aluminum oxide, magnesium aluminum oxide, zinc aluminum oxide, magnesium titanium oxide, iron titanium oxide, calcium titanium oxide, and mixtures thereof.

The inorganic fillers are preferably nonreactive, and may be incorporated into the liquid jet or aerosol jet coating composition in the form of particles, preferably with a particle

size distribution that is the same or smaller than that of the blend of one or more polymer particles.

One or more inorganic fillers may be present in a liquid jet or aerosol jet coating composition of the present disclosure in an amount of at least 0.1 wt-%, at least 1 wt-%, or at least 2 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). One or more inorganic fillers may be present in an amount of up to 20 wt-%, up to 15 wt-%, or up to 10 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). The concentrations in the hardened coating are equivalent to the concentrations of the starting materials in the liquid jet or aerosol jet coating composition.

In some embodiments, one or more pre-prepared surfactants can be used to disperse the polymer particles. In embodiments in which one or more pre-prepared surfactants are used to disperse the polymer particles, the surfactant can be an anionic, a cationic or a zwitterionic surfactant, or a mixture thereof, and also preferably includes one or more salt groups. In preferred embodiments, the surfactant includes one or more neutralized acid or anhydride groups. Examples of suitable neutralized acid groups may include carboxylate groups (COO^-), sulfate groups ($-\text{OSO}_3^-$), sulfinate groups ($-\text{SOO}^-$), sulfonate groups ($-\text{SO}_2\text{O}^-$), phosphate groups ($-\text{OPO}_3^-$), phosphinate groups ($-\text{POO}^-$), phosphonate groups ($-\text{PO}_3^-$), and combinations thereof.

Anionic surfactants are preferred in some embodiments. Examples of suitable anionic surfactants include any of the following surfactants, which preferably have been at least partially neutralized with a suitable base (e.g., any of the bases disclosed herein): any of the acid- or anhydride-functional polymeric surfactants disclosed herein, dodecylbenzene sulfonic acid, dinonylnaphthalene sulfonic acid, dinonylnaphthylenedisulfonic acid, bis(2-ethylhexyl)sulfosuccinic acid, dioctyl sulfosuccinic acid, sodium lauryl sulfate, sodium dodecyl sulfate, sodium laureth sulfate, fatty acid (ester) sulfonate, polyaryl ether phosphate acid or sulfonate acid, and the like, including mixtures thereof.

In some embodiments, it may be useful to use a surfactant that is a “strong acid” surfactant prior to neutralization. Examples of “strong acid” surfactants include surfactants having a pK_a of less than 4 prior to neutralization.

Although any suitable base may be used to neutralize or partially neutralize polymeric or non-polymeric surfactants to form anionic salt groups, amines are preferred bases, with tertiary amines being particularly preferred. Some examples of suitable tertiary amines are trimethyl amine, dimethylethanol amine (also known as dimethylamino ethanol),

methyldiethanol amine, triethanol amine, ethyl methyl ethanol amine, dimethyl ethyl amine, dimethyl propyl amine, dimethyl 3-hydroxy-1-propyl amine, dimethylbenzyl amine, dimethyl 2-hydroxy-1-propyl amine, diethyl methyl amine, dimethyl 1-hydroxy-2-propyl amine, triethyl amine, tributyl amine, N-methyl morpholine, and mixtures thereof. Most preferably triethyl amine or dimethyl ethanol amine is used as the tertiary amine.

Some additional examples of neutralizing bases for forming anionic salt groups include inorganic and organic bases such as sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, and mixtures thereof.

Some examples of neutralizing compounds for neutralizing base groups present on the surfactant and forming cationic salt groups include organic and inorganic acids such as formic acid, acetic acid, hydrochloric acid, sulfuric acid, and combinations thereof.

Although the surfactant may optionally include one or more ethylenically unsaturated groups (e.g., if the surfactant is a polymerizable non-polymeric surfactant), in some embodiments, the surfactant is a saturated surfactant. By way of example, amine-neutralized dodecylbenzenesulfonic acid is considered to be a saturated surfactant. Although amine-neutralized dodecylbenzenesulfonic acid includes an aryl group that includes carbon-carbon double bonds, it does not include any ethylenically unsaturated groups.

The surfactant can be any suitable type of surfactant and may, for example, be a “lower” molecular-weight surfactant (e.g., a surfactant that is non-polymeric and/or has a number average molecular weight of less than about 1,000 Daltons, more typically less than about 750 Daltons, and even more typically less than about 500 Daltons).

In certain preferred embodiments, a polymeric surfactant is used which has, for example, a number average molecular weight greater than about 2,000 Daltons or even greater than about 4,000 Daltons. It is generally preferable to use a polymeric surfactant and/or a polymerizable surfactant to, for example, minimize or eliminate the possibility of surfactant migrating out of the cured coating and into the packaged product. Examples of suitable polymeric surfactants may include water-dispersible polymers of the acrylic, alkyd, polyester, polyether, polyolefin, or polyurethane type, including copolymers thereof (e.g., polyether-acrylic copolymers), and mixtures thereof. Typically, such water-dispersible polymers include one or more salt groups to facilitate stable dispersion into water. Examples of suitable such polymer salts are disclosed in U.S. Pat. No. 8,092,876 (O’Brien et al.), International Pub. No. WO 2018/013766 (Valspar Sourcing), and U.S. Pub. No. 2016/024325 (Li), which describes the use of certain (poly)ethylene (meth)acrylic acid copolymers.

An example of a specific water-dispersible polymer for use as a “polymeric surfactant” is a “higher” acid number acid-functional polymer (e.g., acid number greater than about 40, more preferably greater than about 100 milligrams KOH per gram polymer). In a preferred embodiment, an acrylic polymer having such an acid number is solution
 5 polymerized in organic solvent and then inverted into water (e.g., via at least partial neutralization with a suitable base such as, e.g., an amine or any of the other bases disclosed herein) and used to support emulsion polymerization of the ethylenically unsaturated monomer component. In some embodiments, the acid- or anhydride-functional organic solution polymerized acrylic polymer is formed from an ethylenically unsaturated monomer
 10 component that includes an acid- or anhydride functional monomer, a branched and/or cyclic monomer, and optionally any other suitable ethylenically unsaturated monomer. In some such embodiments, the acrylic polymer is styrene-free.

A variety of acid- or anhydride-functional monomers, or salts thereof, can be used; their selection is dependent on the desired final polymer properties. Preferably, such
 15 monomers are ethylenically unsaturated, more preferably, alpha, beta-ethylenically unsaturated. Suitable ethylenically unsaturated acid- or anhydride-functional monomers include monomers having a reactive carbon-carbon double bond and an acidic or anhydride group, or salts thereof. Preferred such monomers have from 3 to 20 carbons, at least 1 site of unsaturation, and at least 1 acid or anhydride group, or salt thereof.

Suitable acid-functional monomers include ethylenically unsaturated monobasic and
 20 dibasic acids, as well as anhydrides and monoesters of dibasic acids. The selected monomers preferably are readily copolymerizable with any other monomer(s) used to prepare the water-dispersible polymer. Illustrative monobasic acids include those represented by the formula $\text{CH}_2=\text{C}(\text{R}^8)-\text{COOH}$, where R^8 is hydrogen or an alkyl group of 1 to 6 carbon atoms, more
 25 typically hydrogen or methyl ($-\text{CH}_3$).

Examples of useful ethylenically unsaturated acid-functional monomers include acids such as, for example, acrylic acid, methacrylic acid, alpha-chloroacrylic acid, alpha-cyanoacrylic acid, crotonic acid, alpha-phenylacrylic acid, beta-acryloxypropionic acid, fumaric acid, maleic acid, sorbic acid, alpha-chlorosorbic acid, angelic acid, cinnamic acid, p-
 30 chlorocinnamic acid, beta-stearylacrylic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, tricarboxyethylene, 2-methyl maleic acid, itaconic acid, 2-methyl itaconic acid, methyleneglutaric acid, and the like, or mixtures thereof. Preferred unsaturated acid-functional monomers include acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, 2-methyl maleic acid, itaconic acid, 2-methyl itaconic acid, and mixtures thereof.

More preferred unsaturated acid-functional monomers include acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, itaconic acid, and mixtures thereof. Most preferred unsaturated acid-functional monomers include acrylic acid, methacrylic acid, maleic acid, crotonic acid, and mixtures thereof. If desired, aqueous salts of the above acids may also be employed.

Examples of suitable ethylenically unsaturated anhydride monomers include compounds derived from the above acids (e.g., as a pure anhydride or mixtures of such). Preferred anhydrides include acrylic anhydride, methacrylic anhydride, and maleic anhydride.

Examples of suitable polymerizable surfactants include those disclosed in U.S. Pub. No. 2002/0155235 (Taylor et al.); and those commercially available under the tradename REASOAP from Adeka Corporation, Tokyo, Japan; under the tradenames NOIGEN and HITENOL from Da-Ichi Kogyo Siyyaku Co., Ltd., Tokyo, Japan; and under the tradename SIPOMER from Solvay Rhodia, Brussels, Belgium.

In some embodiments, a non-ionic surfactant is included in the reaction mixture used to make the latex polymer. Any suitable non-ionic surfactant may be employed. Examples of suitable non-ionic surfactants include ethoxylated compounds. In some embodiments, the non-ionic compound is a sucrose ester, sorbitan ester, alkyl glycoside, glycerol ester, or mixture thereof. In some embodiments, a non-ionic surfactant is used that includes hydroxyl groups. Non-ionic surfactants that comprise, or are derived from, polysorbate compounds may be used in some embodiments.

In some embodiments, a surfactant or mixture of surfactants as described in U.S. Pub. No. 2020/385601 (Gibanel et al.) may be used. For example, one or more anionic or zwitterionic surfactant (e.g., non-polymeric surfactant) having an acid group neutralized with a metallic base may be used (e.g., a metallic base including aluminum, calcium, lithium, magnesium, sodium, or potassium). An example of such a surfactant is dioctyl sodium sulfosuccinate.

One or more surfactants may be present in a liquid jet or aerosol jet coating composition of the present disclosure in an amount of at least 0.1 wt-%, or at least 0.2 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). One or more surfactants may be present in an amount of up to 10 wt-%, or up to 5 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Standard methods of mixing may be used to form the water-based dispersions.

Coated Metal Substrates

The present disclosure also provides a coated metal substrate. The metal substrate is preferably of suitable thickness to form a metal food or beverage container (e.g., can), an aerosol container (e.g., can), a general packaging container (e.g., can), or a closure, e.g., for a glass jar. The metal substrate has an average thickness of up to 635 microns, preferably up to 375 microns. Preferably, the metal substrate has an average thickness of at least 125 microns. In embodiments in which a metal foil substrate is employed in forming, e.g., a packaging article, the thickness of the metal foil substrate may be even thinner than that described above.

Such metal substrate has a hardened adherent coating disposed on at least a portion of a surface thereof. The hardened adherent coating is formed from a metal packaging (e.g., a food, beverage, or aerosol can) liquid jet or aerosol jet coating composition as described herein with or without one or more optional additives.

Hardened (e.g., cured) coatings of the disclosure preferably adhere well to metal (e.g., steel, stainless steel, electrogalvanized steel, tin-free steel (TFS), tin-plated steel, electrolytic tin plate (ETP), aluminum, etc.). They also provide high levels of resistance to corrosion or degradation that may be caused by prolonged exposure to, for example, food, beverage, or aerosol products.

Thus, metal substrates useful herein include steel, stainless steel, electrogalvanized steel, tin-free steel (TFS), tin-plated steel, electrolytic tin plate (ETP), aluminum, etc. Metal substrates useful herein also includes tab stock and aluminum coil for making beverage can ends (with the hardened coating applied to an interior or exterior surface of the beverage can end, or both. Metal substrates herein may be provided in a coil or sheet form. Metal substrates herein may be provided as a preformed container (e.g., can or cup). If the metal substrate is a preformed can or cup, it can be coated, e.g., by placing it on a spinning mandrel and directing a liquid jet or aerosol jet coating composition to the can or cup while it is spinning. Examples of metal cups that may benefit from coating compositions of the present disclosure are those described in U.S. Pat. No. 10,875,076 (Scott) and U.S. Pub. No. 2019/0112100 (Scott).

In the context of a hardened adherent coating being disposed “on” a surface or substrate, both coatings applied directly (e.g., virgin metal or pre-treated metal such as electroplated steel) or indirectly (e.g., on a primer layer) to the surface or substrate are included. Thus, for example, a coating applied to a pre-treatment layer (e.g., formed from a

chrome or chrome-free pretreatment) or a primer layer overlying a substrate constitutes a coating applied on (or disposed on) the substrate.

If a steel sheet is used as the metal substrate, the surface treatment may comprise one, two, or more kinds of surface treatments such as zinc plating, tin plating, nickel plating, electrolytic chromate treatment, chromate treatment, and phosphate treatment. If an aluminum sheet is used as the metal substrate, the surface treatment may include an inorganic chemical conversion treatment such as chromic phosphate treatment, zirconium phosphate treatment, or phosphate treatment; an organic/inorganic composite chemical conversion treatment based on a combination of an inorganic chemical conversion treatment with an organic component as exemplified by a water-soluble resin such as an acrylic resin or a phenol resin, and tannic acid; or an application-type treatment based on a combination of a water-soluble resin such as an acrylic resin with a zirconium salt.

The metal substrate may be cryogenically cleaned. It may be provided as a cryogenically cleaned metal substrate, or the method coating may include cryogenically cleaning the metal substrate prior to directing a liquid jet or aerosol jet coating composition to at least a portion of the metal substrate. In an exemplary process, cryogenic cleaning may be achieved by directing a high-pressure stream of liquid nitrogen (between 5,000 and 50,000 psi and between 150°F and 250°F) at the metal surface. The temperature of the metal surface decreases rapidly, causing fracturing of any contaminants. The fractured contaminants are then directed away from the metal surface by the high-pressure stream, leaving behind a cleaned substrate.

In preferred embodiments, the hardened adherent coating is continuous. As such, it is free of pinholes and other coating defects that result in exposed substrate, which can lead to (i) unacceptable corrosion of the substrate, and can even potentially lead to a hole in the substrate and product leakage, and/or (ii) adulteration of the packaged product. Except in embodiments in which coating roughness or texture is desired (e.g., for certain exterior can coatings for aesthetic purposes), the hardened continuous coating is preferably smooth, especially for most interior can coatings.

In certain embodiments, the hardened, preferably continuous, adherent coating has an average total thickness of up to 100 microns (particularly if the coating has texture), or a maximum total thickness, up to 100 microns. Typically, however, one or both of the maximum and average total thickness will be appreciably thinner than 100 microns. Preferably, the hardened, preferably continuous, adherent coating has an average total thickness of up to 50 microns, more preferably up to 25 microns, even more preferably up to

20 microns, still more preferably up to 15 microns, and most preferably up to 10 microns, or in certain situations, up to 5 microns. Interior can coatings are typically less than 10 microns thick (total) on average. Preferably, the hardened adherent coating has an average total thickness, or a minimum coating thickness, of at least 1 micron, at least 2 microns, at least 3
5 microns, or at least 4 microns.

The hardened coatings may be used as coatings on any suitable surface, including inside surfaces of metal packaging containers (e.g., food, beverage, or aerosol can bodies, such as three-piece aerosol cans or aluminum monobloc aerosol cans, as well as two-piece and three-piece food or beverage cans), outside surfaces of such container bodies, riveted can
10 ends, pull tabs, and combinations thereof. The hardened coatings may also be used on interior or exterior surfaces of other packaging containers, or portions thereof, metal closures (e.g., for glass containers) including bottle crowns, recyclable aluminum beverage cups such as those commercially available from the Ball Corporation, or metered dose inhaler (MDI) cans. Such specific cans, cups, and other containers, with interior food-contact surfaces,
15 riveted can ends, and pull tabs have specific flexibility requirements, as well as taste, toxicity, and other government regulatory requirements.

The liquid jet or aerosol jet coating compositions of the present disclosure may also be used on substrates other than rigid metal substrate, including substrates for use in packaging food or beverage products or other products. For example, the liquid jet or aerosol
20 jet coating compositions may be used to coat the interior or exterior surfaces of metal or plastic pouches or other flexible packaging. The liquid jet or aerosol jet coating compositions may also be used to coat fiberboard or paperboard (e.g., as employed for Tetra Pack containers and the like); various plastic containers (e.g., polyolefins), wraps, or films; metal foils; or glass (e.g., exteriors of glass bottles to prevent scratching or provide desired color or
25 other aesthetic effects).

The hardened coating preferably includes less than 50 ppm, less than 25 ppm, less than 10 ppm, or less than 1 ppm, extractables, if any, when tested pursuant to the Global Extraction Test described in the Test Methods. Significantly, such coatings are suitable for use on food-contact surfaces. Thus, a metal packaging container (e.g., a food, beverage, or
30 aerosol can) is provided that includes such coated metal substrate, particularly wherein the coated surface of the metal substrate forms an interior surface of the container body (which contacts a food, beverage or aerosol product). Alternatively, the coated surface is a surface of a riveted can end and/or a pull tab.

In certain embodiments, the metal substrate is in the form of a planar coil or sheet, although for side-seam stripes or other applications in which the can has already been formed the metal substrate may not be planar (e.g., it may be in cylindrical form).

Sheet coating involves applying a coating composition to separate pieces of a substrate that has been pre-cut into square or rectangular “sheets.” Coil coating is a special application method in which coiled metal strips (e.g., aluminum) are unwound and then passed through pretreating, coating, and drying equipment before finally being rewound. It is believed the use of preferred liquid jet or aerosol jet coating compositions of the present disclosure can eliminate the need for the pretreatment step employed when using conventional liquid coatings, thereby simplifying the application process and removing cost. Coil coating allows for very efficient coating of large surface areas in a short time at high throughput.

For example, the moving surface of a coil substrate in a continuous process is preferably traveling at a line speed of at least 50 meters per minute, at least 100 meters per minute, at least 200 meters per minute, or at least 300 meters per minute. Typically, the line speed will be less than 400 meters per minute. The curing time of the coil coating applied coating compositions is preferably at least 0.5 second, at least 3 seconds, at least 6 seconds, at least 10 seconds, or at least 12 seconds, and up to 20 seconds, up to about 25 seconds, or up to about 30 seconds. In the context of thermal bakes to cure the coil coating, such curing times refer to the residence time in the oven(s). In such embodiments, the curing process is typically conducted to achieve peak metal temperatures of 200°C to 260°C.

Thus, the process of applying a liquid jet or aerosol jet coating composition to a substrate according to the present disclosure is preferably used in a coil-coating process or in a sheet-coating process.

The hardened coating may be formed from a metal packaging liquid jet or aerosol jet coating composition as described herein with or without one or more optional additives, particularly one with the polymer particles described herein and a lubricant. The lubricant may be present in the hardened coating in the polymer particles, on the polymer particles, in another ingredient used to form the liquid jet or aerosol jet coating composition (or the hardened coating formed therefrom), or a combination thereof. Alternatively or additionally, a lubricant as described herein (e.g., carnauba wax, synthetic wax, polytetrafluoroethylene wax, polyethylene wax, polypropylene wax, or a combination thereof) may be incorporated into or on the hardened coating, a lubricant is preferably present in an amount of at least 0.1 wt-% (or at least 0.5 wt-%, or at least 1 wt-%), and a lubricant is preferably present in an

amount of up to 4 wt-% (or up to 3 wt-%, or up to 2 wt-%), based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating). The concentrations in the hardened coating are equivalent to the concentrations of the starting materials in the liquid jet or aerosol jet coating composition.

5 Preferably, a hardened coating, which includes an amorphous polymer (and/or semicrystalline polymer with amorphous portions), has a glass transition temperature (T_g) of at least 15°C, at least 20°C, or at least 25°C and a T_g of up to 150°C, up to 125°C, up to 110°C, up to 100°C, up to 80°C, or up to 50°C. For many packaging technologies, especially for interior can coatings for more aggressive products, higher T_g coatings are preferred for
10 corrosion resistance.

The hardened coating may not have any detectable T_g.

Preferably, a hardened coating produced from preferred embodiments of the liquid jet or aerosol jet coating composition is capable of passing a 4T T-Bend test when disposed on conventional aluminum beverage can end stock at a conventional average dry film coating
15 weight for an interior beverage can coating (e.g., about 2.3 grams per square meter for an interior soda beverage can coating). A useful T-bend testing procedure is described in ASTM D4145-10 (2010, Reapproved 2018).

Flexibility is especially important for a hardened coating on a metal substrate that is fabricated into a metal packaging container (e.g., a food, beverage, or aerosol can) or part of
20 the container (e.g., can or cup), such as a riveted can end or pull tab. Flexibility is important so that the coating can deflect with the metal substrate during post-cure fabrication steps (e.g., necking and dome reformation, or rivet formation), or if the can is dropped from a reasonable height during transport or use.

Flexibility can be determined using the Flexibility Test described in the Test Methods,
25 which measures the ability of a coated substrate to retain its integrity as it undergoes the formation process necessary to produce a riveted beverage can end. It is a measure of the presence or absence of cracks or fractures in the formed end. Preferably, a hardened coating formed from a coating composition described herein passes this Flexibility Test. In certain embodiments, a preferred coating composition, when applied to a cleaned and pretreated
30 aluminum panel and subjected to a curative bake for an appropriate duration to achieve a 242°C peak metal temperature (PMT) and a dried film thickness of approximately 7.5 milligram per square inch and formed into a fully converted 202 standard opening beverage can end, passes less than 5 milliamps of current while being exposed for 4 seconds to an electrolyte solution containing 1% by weight of NaCl dissolved in deionized water.

The coating should be flexible enough that a coated metal sheet can pass the Fabrication Test with at least a $>7/10$, more preferably $>8/10$, and most preferably $>9/10$ for crazing.

5 The coating should score >100 , more preferably >500 , and most preferably >1000 cycles on the Taber Abrasion Test.

Coated metal substrates of the present disclosure may be drawn and redrawn. Significantly, the coating on the resultant thinned metal substrate remains continuous and adherent.

Methods of Coating

10 The present disclosure provides methods of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, metal closure, or pull tab for an easy open end). This method uses any of the variety of liquid jet or aerosol jet coating compositions, including polymer particles and optional additives, and any of the general systems and methods
15 described herein. The general descriptions of the coatings also apply to the coatings that result from this method.

For example, in one embodiment, a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can), portion thereof, or metal closure) is provided. The method includes:
20 providing a metal packaging liquid jet or aerosol jet coating composition as described herein; directing the liquid jet or aerosol jet coating composition to at least a portion of the metal substrate; and providing conditions effective for the liquid jet or aerosol jet coating composition to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate.

25 In another embodiment, a coating method includes: providing a metal substrate; providing a metal packaging liquid jet or aerosol jet coating composition as described herein; selectively applying the liquid jet or aerosol jet coating composition on at least a portion of the metal substrate to form a patterned coating; and providing conditions effective for the liquid jet or aerosol jet coating composition to form a hardened adherent patterned coating on
30 at least a portion of the metal substrate. This is a method of selectively applying or printing the liquid jet or aerosol jet coating composition.

In another embodiment, a coating method includes applying multiple layers of liquid jet or aerosol jet coating compositions disclosed herein. More than two (for example, three or

more, four or more, or five or more) dissimilar liquid jet or aerosol jet coating compositions may be applied to make a hardened multi-layer coating. The dissimilar liquid jet or aerosol jet coating compositions typically will differ with respect to at least one physical or chemical properties. Representative such properties may include polymer particle properties such as molecular weight, density, glass transition temperature (T_g), melting temperature (T_m), intrinsic viscosity (IV), melt viscosity (MV), melt index (MI), crystallinity, arrangement of blocks or segments, availability of reactive sites, reactivity, acid number, as well as coating composition properties such as surface energy, hydrophobicity, oleophobicity, moisture or oxygen permeability, transparency, heat resistance, resistance to sunlight or ultraviolet energy, adhesion to metals, color or other visual effects, and recyclability. For properties measured on an absolute scale, the dissimilar properties (i.e., a particular property of at least two different liquid jet or aerosol jet coating compositions) may, for example, differ by at least $\pm 5\%$, at least $\pm 10\%$, at least $\pm 15\%$, at least $\pm 25\%$, at least $\pm 50\%$, at least $\pm 100\%$, or more.

Thus, in one embodiment, the present disclosure provides a method of coating a metal substrate suitable for use in forming metal packaging that includes: providing a metal substrate; providing multiple metal packaging liquid jet or aerosol jet coating compositions, wherein at least two of the multiple metal packaging liquid jet or aerosol jet coating compositions are different; directing each of the multiple coating compositions to at least a portion of the metal substrate such that at least one coating composition is deposited on another different coating composition (either prior to or after hardening of the underlying coating composition to form a coating); and providing conditions effective for the multiple liquid jet or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate.

Multi-layer structures are preferably formed using an aerosol jet coating process with partial drying to solidify the sub-layer structures before printing the top layer structure (see, e.g., the multi-layered printed electronic devices produced using aerosol jet printing in *ACS Appl. Mater. Interfaces*, 2014, 6 18704-18711).

The conditions effective for the liquid jet or aerosol jet coating composition to form a hardened coating on at least a portion of the metal substrate preferably includes applying thermal energy (e.g., using a convection oven or induction coil), UV radiation, IR radiation, or electron beam radiation to the liquid jet or aerosol jet coating composition. Such processes can be carried out in one or more discrete or combined steps. The conditions may include applying thermal energy. Applying thermal energy may include using oven temperatures of

at least 100°C or at least 177°C. Applying thermal energy may further include using oven temperatures of up to 300°C or up to 250°C. Applying thermal energy may include heating the coated metal substrate over a suitable time period to a peak metal temperature (PMT) of at least 177°C. Preferably, applying thermal energy includes heating the coated metal

5 substrate over a suitable time period to a peak metal temperature (PMT) of at least 218°C. The time period may be as short as 0.5 second, or less than 1 second, or less than 3 seconds, or 5 seconds, or as long as 15 minutes, preferably less than 12 minutes, and preferably less than one minute for forming a coil coating. Preferably, this occurs in a continuous process.

Methods of coating using a water-based dispersion in a liquid jet or aerosol jet system
10 according to the present disclosure for making metal packaging can be adapted from conventional inkjet printing as described, for example, in U.S. Pat. No. 7,279,506 (Sisler et al.), U.S. Pat. No. 9,428,663 (Song et al.), U.S. Pat. Pub. No. 2008/0062381 (Doshi et al.), and U.S. Pat. Pub. 1004/5938 (Doshi).

Generally, liquid jet coating uses an array of small liquid jets typically controlled by
15 individual piezoelectric valves that turn the flow of the coating composition on or off. Typically, the jet is trained on the surface to be coated, and the piezoelectric valve is controlled by a computer that can either print a monolithic film or a pattern based on the desire of the operator. With this type of application process, the coating remains in the liquid form when it contacts the substrate.

20 Generally, aerosol jet coating converts a liquid coating composition to an aerosol, e.g., using ultrasonic energy. The aerosol is accelerated pneumatically through a small tube and eventually transferred to a substrate through a small nozzle. Significant evaporation occurs during this process, and the coating is largely a solid once it contacts the substrate.

Both liquid jet and aerosol jet coating methods offer significant improvement over
25 traditional roll or spray applied metal packaging coatings.

Methods of Coating a Metal Substrate Using Liquid Jet Coating

A general schematic of an exemplary liquid jet coating system is shown in Fig. 1. Arrow (1) indicates the direction of flow of a water-based dispersion coming from a holding reservoir (not shown). A piezoelectric diaphragm (2) controls the flow of the water-based
30 dispersion to and through a nozzle (3), which is a constricting point where a droplet (4) is generated. The newly generated droplet (4) then moves toward a substrate (5) to be coated. After the droplet (4) is applied to the substrate (5), it flows or wets out the substrate forming a portion of a liquid-jet applied coating (6).

The printheads described herein may be used to apply coating compositions of the present disclosure, as well as any other suitable printheads capable of providing liquid jet or aerosol jet coating known in the art. One set of preferred printheads may be referred to as Drop-on-Demand (DoD) printheads and such printheads usually contain multiple nozzles (e.g., 100 to 1000, although specialist printheads may contain only a single nozzle), and instead of drop ejection resulting from external fluid pressure as in continuous inkjet printing (CIJ) printing, the kinetic energy of the drops derive from sources located within the printhead, typically very close to each nozzle.

In one example of a potentially suitable printhead, a DoD squeeze-mode printhead includes of a hollow tube of piezoelectric material controlled by electrical signal. A voltage is applied to the piezoelectric electrodes causing them to contract, squeezing the chamber containing a water-based dispersion and forcing a droplet out of the nozzle.

Another example of a potentially suitable printhead is a DoD bend-mode printhead, which consists of a piezoelectric disk mounted on one side of the ink chamber. The pulsed electrical signal causes the one side of the chamber to flex inwardly, which reduces the volume of the chamber. The sudden reduction in volume generates pressure pulsed required to push a droplet out of the nozzle. Another example of a potentially suitable printhead is a push-mode piezoelectric print head, which includes a piezoelectric rod placed next to the nozzle part of the chamber. The pulsed electrical signal caused the piezoelectric rod to expand and thus squeeze out the ink droplet. Still another example of a potentially suitable printhead is a DoD shear-mode printhead. The shear mode printheads are designed such that shear deformation in the piezoelectric element is used to deform the upper half of the channels. This deformation is mirrored in the lower half of the channel forcing the channel into a chevron shape. Flexing of the channel induces droplet ejection. This is further described in *Circuit World*, 2012, Vol. 38, 4, 193-213.

Among the printheads that may be used to deliver the coatings described herein, many use the deformation of a piezoelectric ceramic element for this purpose, while in other types (e.g., thermal inkjet heads) the pressure pulse which ejects the drop is generated from the expansion of a small bubble of vapor produced by the action of a small electrical heating element on the liquid itself. There are advantages and disadvantages of both types of actuation. Piezoelectric printheads can typically handle a wider range of liquids than thermal printheads (which are restricted to fluids which will satisfactorily vaporize), while the latter can be simpler and cheaper to fabricate. This is further described in *Intl. J. Pharm.*, 2015, 494, 554-567.

Compositions of the current disclosure are particularly well suited for large-format, industrial scale liquid jetting applications, such as the Powercoat technology developed by Archipelago Technology Group Ltd., Cambridge, UK. In the case of this unique print engine, a cylindrical print head, or roll, is employed that contains a multitude (i.e., plurality) of liquid jetting nozzles distributed evenly across the surface of the roll (i.e., cylindrical print head). It is a particular feature of this printing method that higher viscosity fluids (such as those described by the broadest ranges of the current disclosure) can be coated onto a planar substrate. This style of print engine is described in detail in U.S. Pat. Pub. No. 2021/0031221 A1 (Mace).

10 ***Methods of Coating a Metal Substrate Using Aerosol Jet Coating***

A general schematic of an exemplary aerosol jet coating system is shown in Fig. 2 using the Venturi effect. Arrow (7) indicates the direction of flow of a carrier gas used to drive the Venturi mechanism. At region (8), a cross-flow of carrier gas creates a vacuum that draws a water-based dispersion (12) located in a reservoir (15). Turbulence at this intersection generates an aerosol out of the water-based dispersion. Arrow (9) indicates the direction of flow of small aerosol droplets out of the reservoir (15). The aerosol droplets contact a virtual impactor (10) that condenses the aerosol. Arrow (11) indicates the direction of flow of exhaust of excess vapor resulting in a condensed aerosol. Arrow (14) indicates the direction of flow of condensed aerosol to a nozzle (not shown) for application to a substrate. Large condensed droplets of the aerosol contact the wall (13) of the reservoir (15) and return to the bulk water-based dispersion (12) via gravity.

The pneumatic atomization (Venturi effect) technique can be used to generate aerosols to allow for depositing high viscosity liquids (up to 1000 cps). This is described in *Int. J. Adv. Manuf. Technol.*, 2019, 105, 4599-4619.

A general schematic of an exemplary aerosol jet coating system using ultrasonic energy is shown in Fig. 3. In this method, ultrasonic atomization is used to generate droplets of the water-based dispersion. Arrow (16-1) indicates the direction of flow of a carrier gas, which contacts aerosol droplets (17). The aerosol droplets are formed by ultrasonication from a water-based dispersion (18) using an ultrasonic transducer (19). Arrow (16-2) indicates the direction of flow of the generated aerosol droplets to a nozzle (not shown) for application to a substrate. Further details of this system and its operation are described in U.S. Pat. Pub. No. 2005/0156991 (Renn).

In a method that used ultrasonic energy, due to the micron-scale size of the droplets, solvent evaporation occurs rapidly, resulting in a reduction in droplet size. A carrier gas, referred to herein as the aerosol gas, transports the droplets to a deposition head (i.e., nozzle). During transit, two mechanisms can lead to losses – gravitational settling and impingement on tube walls by diffusion. In the deposition head, a sheath gas surrounds the aerosol gas, collimating the beam. As they pass through a deposition head or nozzle, droplets can be diverted from their flow stream due to inertial effects in the narrow, converging nozzle, leading to aerodynamic focusing. Finally, the droplets can be directed towards the substrate in an impinging jet. This process is further described in *Ind. Eng. Chem. Res.*, 2015, 54, 769-779.

A general schematic of an exemplary aerosol jet coating deposition head or nozzle is shown in Fig. 4. Arrow (20) indicates the direction of flow of condensed aerosol coming from a reservoir via ultrasonication/pneumatic atomization. A sheath gas (21), such as dry N₂ (HP grade, 99.998%) accelerates and focuses the condensed aerosol into a stream (23) toward a substrate (22) to be coated. The sheath gas ensures that the aerosol does not contact the walls of the nozzle, resulting in less nozzle fouling and plugging. After the aerosol stream (23) is applied to the substrate (22), it condenses on the substrate forming a portion of an aerosol-jet applied coating (24).

In certain embodiments of methods of the present disclosure, a multi-head apparatus, as described in U.S. Pat. No. 10,328,680 (Pervan) may be used.

Multi-Layer Coating Methods, Systems, and Resultant Products

The present disclosure also provides a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, metal closure, or pull tab for an easy open end) that involves multi-layer coating, generally forming layers of the liquid jet and/or aerosol jet coating compositions disclosed herein. In this context, a multi-layer coating involves applying a liquid or aerosol jet coating composition onto a liquid or aerosol jet coating composition as well as a liquid or aerosol jet composition onto a hardened liquid or aerosol jet coating. This method uses any of the variety of liquid or aerosol jet coating compositions, including polymer particles and additives, and any of the systems and methods described herein. The general descriptions of the coatings also apply to the coatings that result from this method.

Layers containing the disclosed liquid or aerosol jet coating compositions may be combined in a variety of ratios and in any desired order to form the resultant hardened, preferably continuous, adherent coating. For example, first and second dissimilar liquid or aerosol jet coating compositions may be used to form a hardened coating containing from 99 wt-% to 1 wt-% of a first liquid or aerosol jet coating composition and from 1 wt-% to 99 wt-% of a second liquid or aerosol jet coating composition, from 95 wt-% to 5 wt-% of a first liquid or aerosol jet coating composition and from 5 wt-% to 95 wt-% of a second liquid or aerosol jet coating composition, from 90 wt-% to 10 wt-% of a first liquid or aerosol jet coating composition and from 10 wt-% to 90 wt-% of a second liquid or aerosol jet coating composition, or from 80 wt-% to 20 wt-% of a first liquid or aerosol jet coating composition and from 20 wt-% to 80 wt-% of a second liquid or aerosol jet coating composition, etc.

More than two (for example, three or more, four or more, or five or more) dissimilar liquid or aerosol jet coating compositions may be applied to make a hardened multi-layer coating. The dissimilar liquid or aerosol jet coating compositions typically will differ with respect to at least one physical or chemical property. Representative such properties may include polymer particle properties such as molecular weight, density, glass transition temperature (T_g), melting temperature (T_m), intrinsic viscosity (IV), melt viscosity (MV), melt index (MI), crystallinity, arrangement of blocks or segments, availability of reactive sites, reactivity, acid number, as well as coating composition properties such as surface energy, hydrophobicity, oleophobicity, moisture or oxygen permeability, transparency, heat resistance, resistance to sunlight or ultraviolet energy, adhesion to metals, color or other visual effects, and recyclability. For properties measured on an absolute scale, the dissimilar properties (i.e., a particular property of at least two different liquid or aerosol jet coating compositions) may, for example, differ by at least $\pm 5\%$, at least $\pm 10\%$, at least $\pm 15\%$, at least $\pm 25\%$, at least $\pm 50\%$, at least $\pm 100\%$, or more.

Thus, in one embodiment, the present disclosure provides a method of coating a metal substrate suitable for use in forming metal packaging that includes: providing a metal substrate; providing multiple metal packaging liquid or aerosol jet coating compositions, wherein each liquid or aerosol jet coating composition comprises polymer particles, and at least two of the multiple metal packaging liquid or aerosol jet coating compositions are different; directing each of the multiple liquid or aerosol jet coating compositions to at least a portion of the metal substrate such that at least one liquid or aerosol jet coating composition is deposited on another different liquid or aerosol jet coating composition (either prior to or after at least partially hardening of the underlying liquid or aerosol jet coating composition to

form a coating); and providing conditions effective for the multiple liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate. At least partially hardening (e.g., by heating) the underlying coating composition is preferred to at least partially remove liquid (e.g., organic solvent or water) to resist impact of the of the subsequently applied coating composition and avoid mixing the layered coating compositions.

Although the method can involve providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating between depositing layers of different liquid or aerosol jet coating compositions, preferably the method involves providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating after depositing all the layers of different liquid or aerosol jet coating compositions.

A particular advantage of applying multiple different metal packaging liquid or aerosol jet coating compositions is that each composition can be chemically different and/or physically different, and provide a specific function that would otherwise be difficult to achieve with a single material. For example, hardness and flexibility can be quite difficult to achieve in a single coating composition, because they are achieved by incorporating dissimilar functionalities and architectures into the polymer backbone of the coating. Moreover, relative to conventional multi-layer packaging coating approaches (e.g., using conventional liquid applied coating approaches for each layer such as roll coating, spray coating, and the like), performance enhancements and/or cost savings can be realized by selectively applying one or more liquid or aerosol jet coating layers in a multi-layer coating system only where that particular layer is desired (e.g., as opposed to “all-over coating” for the given layer).

Fig. 5 provides schematics of representative examples of assemblies that include multilayer coatings in the rigid metal packaging industry. As shown on the left side of the substrate (511) in Fig 5, using this method, a lubricant (513) may be applied in a second liquid or aerosol jet coating composition on a base liquid or aerosol jet layer (512) on substrate (511), prior to cure of the base liquid or aerosol jet layer, only where needed, thereby eliminating the need for applying lubricant globally. In most cases, this lubricant layer will be selectively applied in a patterned format such that it only covers 50% or less of the base liquid or aerosol jet coating layer and/or is typically not thicker than the particle size of the lubricant applied.

In certain embodiments that include multi-layer liquid or aerosol jet coating compositions, each of the compositions do not include lubricant.

As shown in the middle portion of the substrate (511) in Fig. 5, two chemically different liquid or aerosol jet coating compositions may be applied – a first liquid or aerosol jet coating composition (514) may be applied to form a color coating, and then a second (different) liquid or aerosol jet coating composition (515) may be applied to form an outermost (i.e., top) clear coating over the colored coating (514). This can eliminate tool wear issues with pigmented end/tab coatings.

As shown on the right side of the substrate (511) in Fig. 5, a first liquid or aerosol jet coating composition (516) can be applied to provide a relatively soft coating layer, and a second liquid or aerosol jet coating composition (517) can be applied (i.e., deposited) to provide a relatively hard top (i.e., outermost) coating layer. In this context, soft and hard are used as terms to describe the relative hardness or softness (Tg) of the resultant first and second coatings (as opposed to a “hardened” coating). The softer coating (516) provides flexibility and a primer layer which enhances adhesion of the hard top coating layer (517), whereas the harder coating (517) provides an abrasion-resistant top coating.

Another example of multi-layer architectures includes the use of multiple differently colored liquid or aerosol jet coating compositions that can be used in color-on-color printing to generate a new color. Thus, the multiple liquid or aerosol jet coating compositions can include a base set of colors that can be mixed to form other colors. Similar to the way a desktop printer works, a multi-color-plus-black scheme (preferably a three-color-plus-black scheme) could be used to print an infinite array of colors from only four liquid or aerosol jet coating composition sources, typically magenta, cyan, yellow, and black. For color development layers where a preceding or subsequent layer is providing a continuous protective layer over the metal substrate, a pixel approach to achieve an infinite array of colors may be used. In this way, individual pixels or points (sufficiently small so as not to be detected by the human eye), can be printed onto the substrate such that the array of pixels or points on the substrate appear to the human eye to be a result of blending of those colors. For example, a 1:1 blend of cyan and yellow pixels would appear green to the unaided eye.

Mechanically, this array of colors could be achieved by arranging an appropriate number of liquid or aerosol jet coating apparatuses (one for each color) in a row, so that each one deposits a proscribed liquid or aerosol jet coating composition onto the substrate, with each one depositing its coating composition on top of the previous layer.

Yet another example of multi-layer liquid or aerosol jet coating architectures that could be of utility in the rigid metal packaging industry includes the use of a pretreatment base layer. Traditional non-chrome aluminum pretreatments consist of molybdenum and/or zirconium compounds (often in a polyacrylic acid matrix) that are coated in a very thin (sub-micron) layer prior to the protective coating. In some applications, the polyacrylic acid sealer layer provides a significant percentage of the pretreatment performance advantage. This pretreatment process is often complicated and messy. It would be beneficial to use a liquid or aerosol jet coating composition in a very thin layer of a pretreatment metal compound sealer, or potentially just sealer by itself.

A multi-layer liquid or aerosol jet coating architecture may include multiple liquid or aerosol jet coating compositions deposited in a manner to form a textured surface (e.g., detectable by unaided human senses visually and/or by touch). The texture results from the coating being applied to a smooth/flat metal substrate. Alternatively, a multi-layer liquid or aerosol jet coating architecture may include multiple liquid or aerosol jet coating compositions deposited in a manner to form a smooth/flat surface. The smooth/flat surface results from the coating being applied to a smooth/flat metal substrate or a textured substrate. The textured or smooth surface may be detectable to human eye and/or human touch, or alternatively, the texture can be measured and reported as an Arithmetical Mean Roughness (Ra). Arithmetical mean roughness indicates the average of the absolute value along the sampling length and can be measured with, for example, a 3D surface profiler such as the Keyence VK-X3000.

A multi-layer liquid or aerosol jet coating architecture may result in a hardened, preferably continuous, adherent coating that forms markings, as described for the patterned coating method.

A multi-layer liquid or aerosol jet coating architecture may result in a hardened, preferably continuous, adherent coating having different thicknesses across a coated surface as a result of the liquid or aerosol jet coating composition being deposited in different amounts. For example, the hardened adherent coating may have an average total thickness of up to 100 microns, or a maximum total thickness up to 100 microns. Typically, however, one or both of the maximum and average total thickness will be appreciably thinner than 100 microns (e.g., 50 microns or less or 30 microns or less, particularly for liquid jet coating). The coating may have multiple layers of liquid or aerosol jet coating compositions, thereby providing different thicknesses throughout the coating. The highest peak of a cross-section of a coating may be measured using microscopy (e.g., optical microscopy).

In methods of the present disclosure wherein multiple liquid or aerosol jet coating compositions are used, directing each of the multiple liquid or aerosol jet coating compositions comprises directing each of the multiple liquid or aerosol jet coating compositions to at least a portion of the metal substrate.

5 The present disclosure also provides coated metal substrates, and metal packaging that includes such coated metal substrates, having a surface at least partially coated with a coating prepared by methods of the present disclosure wherein multiple liquid or aerosol jet coating compositions are used. Such metal packaging is analogous to that described herein made by the general methods that are described above. Such packaging may be filled with a food,
10 beverage, or aerosol product.

 The present disclosure also provides a packaging coating system, comprising:
multiple metal packaging liquid or aerosol jet coating compositions, wherein at least two of the multiple metal packaging liquid or aerosol jet coating compositions are different; wherein each liquid or aerosol jet coating composition is as described herein. Such systems
15 preferably further include instructions comprising: directing each of the multiple liquid or aerosol jet coating compositions to at least a portion of a metal substrate such that at least one liquid or aerosol jet coating composition is deposited on another different liquid or aerosol jet coating composition (prior to or after at least partially hardening of the prior applied liquid or aerosol jet coating composition); and providing conditions effective for the multiple liquid or
20 aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate.

 Preferably, in such systems, at least two of the metal packaging liquid or aerosol jet coating compositions differ in one or more chemical or physical properties. Such properties include polymer particle properties (such as molecular weight, density, glass transition
25 temperature (T_g), melting temperature (T_m), intrinsic viscosity (IV), melt viscosity (MV), melt index (MI), crystallinity, arrangement of blocks or segments, monomer composition, availability of reactive sites, reactivity, and acid number), and coating composition properties (such as surface energy, hydrophobicity, oleophobicity, moisture or oxygen permeability, transparency, heat resistance, resistance to sunlight or ultraviolet energy, adhesion to metals,
30 color or other visual effects, and recyclability). Preferably, a particular property of at least two different liquid or aerosol jet coating compositions differ by at least $\pm 5\%$, at least $\pm 10\%$, at least $\pm 15\%$, at least $\pm 25\%$, at least $\pm 50\%$, at least $\pm 100\%$, or more.

 In such systems, the multiple liquid or aerosol jet coating compositions are typically contained in a plurality of cartridges, wherein each cartridge of the plurality of cartridges

contains a liquid or aerosol jet coating composition, and wherein at least two cartridges of the plurality of cartridges contain different liquid or aerosol jet coating compositions (e.g., a differently colored liquid or aerosol jet coating composition). Preferably, such cartridges are refillable and reusable.

5 ***Patterned Coating Methods, Systems, and Resultant Products***

The present disclosure also provides a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, metal closure, or pull tab for an easy open end), that involves forming a patterned coating. This method uses any of the variety of liquid or aerosol jet coating compositions, including polymer particles and additives, and any of the general and cartridge-based systems and methods described herein. The general descriptions of the coatings also apply to the coatings that result from this method.

In particular, this method includes: providing a metal substrate; providing a metal packaging liquid or aerosol jet coating composition, wherein the liquid or aerosol jet coating composition comprises polymer particles; selectively applying the liquid or aerosol jet coating composition on at least a portion of the metal substrate to form a patterned coating; and providing conditions effective for the liquid or aerosol jet coating composition to form a hardened adherent patterned coating on at least a portion of the metal substrate. This is a method of selectively applying or printing the liquid or aerosol jet coating composition.

A “patterned” coating (i.e., a multi-portion coating) refers to a hardened coating printed in two or more regions on a substrate surface, which may or may not have blank regions between and/or surrounding the printed regions having no coating thereon.

A patterned coating may include a regular or irregular pattern of coated regions, which may be in a variety of shapes (e.g., stripes, diamonds, squares, circles, ovals, rings). Such coated regions could be very discrete with clearly delineated transitions. Alternatively, such coated regions could provide gradient effects (e.g., in terms of color or matte/gloss) without clearly delineated transitions.

The terms “pattern” and “patterned” do not require any repetition in design elements, although such repetition may be present. The hardened coated regions of the patterned coating are preferably continuous in that they are free of pinholes and other coating defects that result in exposed substrate if an underlying coating is not present.

A patterned coating may be applied on another liquid or aerosol jet coating, whether it is an all-over coating or another patterned coating. A patterned coating may be applied to a conventional liquid-applied base coat.

Using a patterned coating method as described herein has a number of advantages. It provides the ability to do things in a selective and/or differential manner in a given coating, which is different from conventional methods. For example, the patterned coating could provide information in the form of markings. In this context, “markings” includes graphics, text, indicia, numbers, letters, code, communication means (e.g., as to when and where coated), and other visual images (e.g., faces such as those of celebrities, animals, characters, objects, artistic representations, and the like) including high resolution images. The markings could be present as portions within an overall layer, or could be applied as a second layer (i.e., with the edge boundaries of the layer substantially defined by the markings or each individual marking). The markings could be applied, e.g., by a customer, to a conventional continuous liquid-applied base coat already present.

Using a patterned coating method as described herein could result in a potential savings in the amount of liquid or aerosol jet coating composition consumed. There may also be a reduction in the amount of metal substrate scrapped. For example, savings can occur using a patterned coating architecture in the fabrication of paint cans. A ring-shaped coating can be applied to a metal substrate (e.g., steel) only in the area where the ring is to be formed, leaving the remaining metal substrate free of any coating material (i.e., referred to as “bare tinplate”). Once the coated ring is formed the remaining bare tinplate can then be used to create gallon lids. This operation saves on the consumption of the metal substrate by allowing what would have been scrapped to be usable material.

Using a patterned coating method as described herein could result in a potential reduction in down time due to the need to clean fabrication machinery. For example, applying a liquid or aerosol jet coating composition as a patterned (e.g., spot) coating to a product contact area for a food or beverage can end, or similar packaging parts, could prevent the downstream effect of developing coating hairs in the fabrication machinery. In a conventional method, shearing an organic coating on tinplated steel generates a thin hair of coating which is pulled from the cut edge. This coating hair builds up in the machinery, creating a cleanliness issue and down time. Applying a spot coating in the food-contact area only allows for the cut edge to remain free of coating material. This prevents formation of coating hairs and eliminates the down time needed for cleaning and translates into a significant cost savings.

The fabrication of food and beverage can ends is one of the most demanding areas of rigid metal packaging fabrication, due largely to the significant number of fabrication steps that occur after a coating is applied to a metal substrate in a coil format (and sometimes to metal sheets). This is especially true for so called “easy open” food and beverage can ends, which include a “rivet” having extreme contours for purposes of attaching a pull-tab to the can end. With a conventional liquid-based roll coat application, the coating composition needs to be highly engineered to pass the post-coating fabrications steps. Because a significant amount of the can end is subjected to few, if any, of these post-coating fabrication steps, the coating composition is actually over-engineered for these areas. As shown in Fig. 6, a liquid or aerosol jet patterned coating can be provided on only selected regions (602) of the can end (600) as described herein, however, allows these regions (602) of the metal substrate that are subject to the significant number of fabrication steps to be coated with a highly engineered liquid or aerosol jet coating composition with superior flexibility and adhesion, such as one that includes polyester or epoxy polymer particles. Then, a more general-performance liquid or aerosol jet coating composition (604) that includes acrylic polymer particles, for example, can be applied over the entire surface of the can end (600).

The fabrication of metal closures for glass jars (e.g., lugged or threaded caps) will also benefit from a liquid or aerosol jet patterned coating method as described herein. Such metal closures (700) (as shown in Fig. 7) are typically double coated, with the top coat being formulated to have good adhesion to a polyvinyl chloride (PVC) gasket that aids in sealing the lid (i.e., metal closure such as lug cap) to the glass jar. The top coat must also prevent leaching of the PVC plasticizer (found in the gasket) into the base coat and encourage corrosion. Using the liquid or aerosol jet patterned coating methods as described herein, a high-performance, gasket-compatible, liquid or aerosol jet coating composition for the top coat could be localized to a ring shape (702) in the area directly under the gasket, versus being coated over the entire closure (700). Fig. 7 is a schematic of a liquid or aerosol jet patterned coating on one example of a lug cap (700) seen in a perspective view on the left side of Fig. 7, with the upper right cross-sectional view A-A of Fig. 7 being taken along line A-A in the lowermost view of Fig. 7.

Multiple liquid or aerosol jet coating compositions, where at least two of the multiple metal packaging liquid or aerosol jet coating compositions are different, may be used in the patterned coating method, as described for the multi-layer liquid or aerosol jet coating methods. For example, a method could involve directing a liquid or aerosol jet coating composition to at least a portion of a metal substrate to form a continuous coating, which may

be a patterned coating or an all-over coating, before or after forming a patterned coating with a different liquid or aerosol jet composition. For exterior images/printing, currently a patterned coating layer (i.e., a pattern layer) is used that is separate from a protective layer. The patterned coating method would allow for the pattern layer and performance layer to be accomplished in a single pass through the coating apparatus followed by a single hardening step as needed.

In another example that involves a patterned coating method that uses multiple liquid or aerosol jet coating compositions, each of the multiple liquid or aerosol jet coating compositions may be directed to at least a portion of the metal substrate such that at least one liquid or aerosol jet coating composition is optionally deposited on another different liquid or aerosol jet coating composition to form a coating. This could include multi-layer liquid or aerosol jet coatings. Alternatively, the multiple coating compositions could be directed to different, non-overlying areas (e.g., abutting areas that such a continuous coating is preferably formed), which is distinct from the multi-layer methods described herein.

As with the multi-layer liquid or aerosol jet coating methods, providing conditions effective for each of the multiple liquid or aerosol jet coating compositions to form a hardened coating involves providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened coating between depositing layers of different liquid or aerosol jet coating compositions. Preferably, however, the method involves providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened coating after depositing all the layers of different liquid or aerosol jet coating compositions.

A patterned coating may have different thicknesses across a coated surface as a result of the liquid or aerosol jet coating composition being deposited in different amounts, as described for the multi-layer coating method. This is advantageous in the rigid metal packaging industry when there is a need for a varied coating thickness across a substrate surface (i.e., an indexed variable thickness coating) for example, for coating performance and/or aesthetic purposes. Preferably, such coating thickness can be selectively varied on demand during application. Such selectivity cannot be achieved using a conventional roll-applied liquid coating process. To achieve selective variable thicknesses using such conventional process, expensive and permanent milling/etching of the application roll would be required. Furthermore, such conventional process could not provide the high degree of resolution that can be accomplished using a method of the present disclosure.

Fig. 8 demonstrates an example of the utility of an indexed variable thickness (IVT) coating. This illustrates an IVT coating as it could be used in the rigid metal packaging industry to produce a coated metal sheet. From this sheet, can/cup blanks could be punched and subsequently formed through a traditional drawing and ironing process. In the margins (806) between the blanks, which are typically collected and recycled, no coating is applied. In the circular areas (800) separated by the margin (806) that will eventually be punched out for can/cup blanks, more coating can be applied in a radial pattern to the areas (800) that will eventually become the upper sidewall of the can/cup. The depicted circular areas (800) may include indexed coating weights forming concentric circles (802, 803, 804, and 805), with the coating weights increasing when moving from the central portion (802) outward. The thickest coating weights may be found in one or more of the outermost rings (804 and/or 805) where needed at, e.g., upper sidewalls of a can or cup. This is useful because the upper sidewall of the can/cup is typically more susceptible to corrosion than other areas such as the dome or bottom area.

A patterned coating may also have different finishes. For example, at least a portion of the patterned coating may have a glossy finish. Alternatively, at least a portion of the patterned coating may have a matte finish. The patterned coating may have one or more gradient (e.g., gradual) transitions from a glossy finish area (i.e., region) to a matte finish area and/or one or more immediate transitions from a glossy finish area to a matte finish area. Such matte/glossy finishes can be determined using a gloss meter, such as a BYK-Gardner AG-4440 digital gloss meter.

The present disclosure also provides pattern-coated metal substrates, and metal packaging that includes such pattern-coated metal substrates. More specifically, a pattern-coated metal substrate is provided that is suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, metal closure, or pull tab for an easy open end), wherein at least a portion of the metal substrate has a surface coated with a hardened adherent patterned coating comprising liquid or aerosol jet coating compositions. Such metal packaging is analogous to that described herein made by the general methods that describe the use of a single liquid or aerosol jet coating composition. Such packaging may be filled with a food, beverage, or aerosol product.

The present disclosure also provides a packaging coating system for patterned coating, comprising: one or more metal packaging liquid or aerosol jet coating compositions; wherein each liquid or aerosol jet coating composition as described herein; and instructions

comprising: selectively applying the one or more liquid or aerosol jet coating compositions on at least a portion of the metal substrate to form a patterned coating; and providing conditions effective for the one or more liquid or aerosol jet coating compositions to form a hardened adherent patterned coating (which may or may not be continuous) on at least a portion of the metal substrate.

Preferably, in such systems that include at least two different metal packaging liquid or aerosol jet coating compositions, such compositions differ in one or more chemical or physical properties. Such properties include polymer particle properties (such as molecular weight, density, glass transition temperature (T_g), melting temperature (T_m), intrinsic viscosity (IV), melt viscosity (MV), melt index (MI), crystallinity, arrangement of blocks or segments, monomer composition, availability of reactive sites, reactivity, and acid number), and coating composition properties (such as surface energy, hydrophobicity, oleophobicity, moisture or oxygen permeability, transparency, heat resistance, resistance to sunlight or ultraviolet energy, adhesion to metals, color or other visual effects, and recyclability). Preferably, a particular property of at least two different liquid or aerosol jet coating compositions differ by at least $\pm 5\%$, at least $\pm 10\%$, at least $\pm 15\%$, at least $\pm 25\%$, at least $\pm 50\%$, at least $\pm 100\%$, or more.

Metal Packaging and Methods of Making

The present disclosure also provides metal packaging (e.g., a metal packaging container such as a food, beverage, aerosol, or general packaging container (e.g., can or cup), a portion thereof, or a metal closure) that includes a coated metal substrate as described herein. The coated surface of the metal substrate preferably forms an interior surface of the container (e.g., can or cup) or closure (although it can form an exterior surface). The coated surface of the metal substrate is preferably a surface of a riveted can end, a pull tab, and/or a can body. The metal packaging container (e.g., food, beverage, or aerosol can) may be filled with a food, beverage, or aerosol product.

A method of making metal packaging (e.g., a metal packaging container such as a food, beverage, aerosol, or general packaging container (e.g., can), a portion thereof, or a metal closure for a container such as a metal can or glass jar) is provided. The method includes: providing a metal substrate (e.g., coil or sheet) having a hardened, preferably continuous, adherent coating disposed on at least a portion of a surface thereof, wherein: the metal substrate has an average thickness of up to 635 microns; the hardened, preferably continuous, adherent coating is formed from a metal packaging liquid jet or aerosol jet

coating composition; wherein the liquid jet or aerosol jet coating composition comprises polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons, wherein the polymer particles have a particle size distribution having a D50 of less than 10 microns; and forming the substrate (e.g., by stamping) into at least a portion of a metal packaging container (e.g., food, beverage, aerosol, or general packaging can) or a portion thereof, or a metal closure for a container (e.g., metal can or glass jar).

A liquid/aerosol jet coating application process as described herein may be positioned in-line with the fabrication of metal packaging. More specifically, the present disclosure provides a method of making metal packaging (e.g., a metal packaging container such as a food, beverage, aerosol, or general packaging container (e.g., can or cup), a portion thereof, or a metal closure such as for a metal packaging container or a glass jar) in one location and/or in one continuous manufacturing line or process. In one exemplary embodiment, the method includes: providing a metal substrate; providing a metal packaging liquid jet or aerosol jet coating composition as described herein; directing the liquid jet or aerosol jet coating composition to at least a portion of the metal substrate; providing conditions effective for the coating composition to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate; and forming the at least partially coated metal substrate into at least a portion of a metal packaging container (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup)), a portion thereof, or a metal closure (e.g., for a metal packaging container or a glass jar).

While the coating application process is typically completed as a stand-alone process (after the metal coil/sheet is produced and before the packaging container is produced), Fig. 9 depicts the aforementioned, in-line process where the metal coil/sheet production (902) and the coating composition production (904) feed separately into the packaging container production process (906). In this way, one or more embodiments may include the liquid/aerosol jet coating process (910) being done in-line between the substrate preparation process (908) (e.g., a metal coil/sheet unspooler, sheet feeder, etc.) and the packaging container fabrication process (912) (where the packaging container is, e.g., a can, cup, or a portion of packaging container such as, e.g., a lid, cap, etc.).

For example, two-piece or three-piece cans or portions thereof such as stamped riveted beverage can ends (e.g., soda or beer cans) with a hardened coating formed from the liquid jet or aerosol jet coating composition described herein disposed thereon can be formed using such a method. Standard fabrication techniques, e.g., stamping, may be used.

The coated surface of the metal substrate preferably forms an interior surface of a can. The coated surface of the metal substrate is preferably a surface of a riveted can end, a pull tab, and/or a can body. The can may be filled with a food, beverage, or aerosol product.

EXEMPLARY EMBODIMENTS

5 **Embodiments A: Metal Packaging Liquid Jet or Aerosol Jet Coating Compositions**

Embodiment A-1 is a metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can, cup), portion thereof, or metal closure) liquid jet or aerosol jet coating composition comprising: polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons, wherein the polymer particles have a
10 particle size distribution having a D50 of less than 10 microns; and a liquid carrier comprising water in a major amount of the liquid carrier.

Embodiment A-2 is the liquid jet or aerosol jet coating composition of Embodiment A-1, wherein the polymer particles have a particle size distribution having a D50 of less than 5 microns, less than 1 micron, or less than 0.5 micron.

15 Embodiment A-3 is the liquid jet or aerosol jet coating composition of Embodiment A-1 or A-2, wherein the polymer particles have a particle size distribution having a D90 of less than 10 microns, less than 5 microns, less than 1 micron, or less than 0.5 micron.

Embodiment A-4 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles have a particle size distribution
20 having a D95 of less than 10 microns, less than 5 microns, less than 1 micron, or less than 0.5 micron.

Embodiment A-5 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles have a particle size distribution having a D99 of less than 10 microns, less than 5 microns, less than 1 micron, or less than 0.5
25 micron.

Embodiment A-6 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles have a particle size distribution having a D50 (preferably, a D90, D95, or a D99) of at least 0.01 micron, at least 0.05 micron, or at least 0.1 micron.

30 Embodiment A-7 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments having a solids content of at least 10 wt-%, at least 15 wt-%, or at least 20 wt-%, based on the total weight of the coating composition (prior to incorporating into a liquid jet or aerosol jet coating system).

Embodiment A-8 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments having a solids content of up to 50 wt-%, up to 40 wt-%, or up to 30 wt-%, based on the total weight of the coating composition (prior to incorporating into a liquid jet or aerosol jet coating system).

5 Embodiment A-9 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments comprising at least 30 wt-%, at least 50 wt-%, or at least 70 wt-%, of the polymer particles, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

10 Embodiment A-10 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments comprising up to 99 wt-%, up to 97 wt-%, or up to 95 wt-%, of the polymer particles, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

15 Embodiment A-11 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the viscosity of the coating composition for a liquid jet application process is preferably at least 1 centipoise (cps), at least 10 cps, or at least 20 cps.

Embodiment A-12 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the viscosity of the coating composition for a liquid jet application process is preferably up to 50 centipoise (cps), up to 40 cps, or up to 30 cps.

20 Embodiment A-13 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the viscosity of the coating composition for an aerosol jet application process is preferably at least 1 centipoise (cps), at least 50 cps, or at least 100 cps.

Embodiment A-14 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the viscosity of the coating composition for an aerosol jet application process is preferably up to 1,000 centipoise (cps), up to 500 cps, or up to 200 cps.

25 Embodiment A-15 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the surface tension of the coating composition for a liquid or aerosol jet application process is at least 10 milliNewtons per meter (mN/m), at least 20 mN/m, or at least 30 nM/m.

30 Embodiment A-16 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the surface tension of the coating composition for a liquid or aerosol jet application process is up to 50 mN/m, up to 45 mN/m, or up to 40 mN/m.

Embodiment A-17 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a thermoplastic polymer.

Embodiment A-18 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a polymer having a melt flow index (measured pursuant to ASTM D1238-13 (2013) at 190°C and with a 2.16-kilogram weight) of greater than 15 grams/10 minutes, greater than 50 grams/10 minutes, or greater than 100 grams/10 minutes.

Embodiment A-19 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a polymer having a melt flow index of up to 200 grams/10 minutes, or up to 150 grams/10 minutes.

Embodiment A-20 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a thermoset polymer.

Embodiment A-21 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a polymer having a glass transition temperature (T_g) of at least 15°C, at least 20°C, or at least 25°C.

Embodiment A-22 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a polymer having a T_g of up to 150°C, up to 125°C, up to 110°C, up to 100°C, up to 80°C, or up to 50°C.

Embodiment A-23 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a crystalline or semi-crystalline polymer having a melting point of at least 40°C.

Embodiment A-24 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a crystalline or semi-crystalline polymer having a melting point of up to 300°C.

Embodiment A-25 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer particles comprise a polymer selected from a polyacrylic (e.g., a solution-polymerized acrylic polymer, an emulsion polymerized acrylic polymer, or combination thereof), polyether, polyolefin, polyester, polyurethane, polycarbonate, polystyrene, or a combination thereof (i.e., copolymer or mixture thereof such as polyether-acrylate copolymer). Preferably, the polymer is selected from a polyacrylic, polyether, polyolefin, polyester, or a combination thereof.

Embodiment A-26 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer Mn is at least at least 3,000 Daltons or at least 4,000 Daltons.

Embodiment A-27 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer Mn is up to 60,000 Daltons.

Embodiment A-28 is the liquid jet or aerosol jet coating composition of Embodiment A-27, wherein the polymer Mn is up to up to 40,000 Daltons or up to 20,000 Daltons.

Embodiment A-29 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments, wherein the polymer has a polydispersity index (Mw/Mn) of less than 4, less than 3, less than 2, or less than 1.5.

Embodiment A-30 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments further comprising one or more optional additives selected from lubricants, adhesion promoters, crosslinkers, catalysts, colorants (e.g., pigments or dyes), ferromagnetic particles, degassing agents, levelling agents, wetting agents, matting agents, surfactants, flow control agents, heat stabilizers, anti-corrosion agents, adhesion promoters, inorganic fillers, and combinations thereof.

Embodiment A-31 is the liquid jet or aerosol jet coating composition of Embodiment A-30 further comprising one or more colorants.

Embodiment A-32 is the liquid jet or aerosol jet coating composition of Embodiment A-31, wherein the one or more colorants are present in the liquid jet or aerosol jet coating composition in an amount of at least 1 wt-%, at least 2 wt-%, at least 5 wt-%, at least 10 wt-%, or at least 15 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-33 is the liquid jet or aerosol jet coating composition of Embodiment A-31 or A-32, wherein the one or more colorants are present in the liquid jet or aerosol jet coating composition in an amount of up to 50 wt-%, up to 40 wt-%, up to 30 wt-%, or up to about 20%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-34 is the liquid jet or aerosol jet coating composition of any of Embodiments A-30 through A-33 further comprising one or more lubricants.

Embodiment A-35 is the liquid jet or aerosol jet coating composition of Embodiment A-34, wherein the one or more lubricants are present in the liquid jet or aerosol jet coating composition in an amount of at least 0.1 wt-%, at least 0.5 wt-%, or at least 1 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-36 is the liquid jet or aerosol jet coating composition of Embodiment A-34 or A-35, wherein the one or more lubricants are present in the liquid jet or aerosol jet coating composition in an amount of up to 4 wt-%, up to 3 wt-%, or up to 2 wt-%, based on

the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-37 is the liquid jet or aerosol jet coating composition of any of Embodiments A-30 through A-36 further comprising one or more crosslinkers and/or catalysts.

Embodiment A-38 is the liquid jet or aerosol jet coating composition of Embodiment A-37 comprising one or more crosslinker in an amount of at least 0.1 wt-%, at least 1 wt-%, at least 2 wt-%, at least 5 wt-%, or at least 8 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-39 is the liquid jet or aerosol jet coating composition of Embodiment A-37 or A-38 comprising one or more crosslinkers in an amount of up to 40 wt-%, up to 30 wt-%, up to 20 wt-%, or up to 10 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-40 is the liquid jet or aerosol jet coating composition of any of Embodiments A-37 through A-39 comprising one or more catalysts in an amount of at least 0.01 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-41 is the liquid jet or aerosol jet coating composition of any of Embodiments A-37 through A-40 comprising one or more catalysts in an amount of up to 5 wt-%, based on the total solids content of the coating composition (i.e., the total weight of the overall hardened coating).

Embodiment A-42 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments which is substantially free of each of bisphenol A, bisphenol F, and bisphenol S.

Embodiment A-43 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments which is substantially free of all bisphenol compounds, except for TMBPF (which may be optionally present as a structural unit).

Embodiment A-44 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments which forms a coating that includes less than 50 ppm, less than 25 ppm, less than 10 ppm, or less than 1 ppm, extractables, if any, when tested pursuant to the Global Extraction Test.

Embodiment A-45 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments which forms a coating that adheres to a substrate, such as a metal substrate, according to the Adhesion Test with an adhesion rating of 9 or 10, preferably 10.

Embodiment A-46 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments which forms a hardened, preferably continuous, coating that is free of pinholes and other coating defects that result in exposed substrate. Such film

imperfections/failures can be indicated by a current flow measured in milliamps (mA) using the Flat Panel Continuity Test described in the Test Methods.

Embodiment A-47 is the liquid jet or aerosol jet coating composition of any of the preceding embodiments which, when applied to a cleaned and pretreated aluminum panel and subjected to a curative bake for an appropriate duration to achieve a 242°C peak metal temperature (PMT) and a dried film thickness of approximately 7.5 milligram per square inch and formed into a fully converted 202 standard opening beverage can end, passes less than 5 milliamps of current while being exposed for 4 seconds to an electrolyte solution containing 1% by weight of NaCl dissolved in deionized water.

Embodiments B: Methods of Coating a Metal Substrate and Coated Metal Substrates

Embodiment B-1 is a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can), portion thereof, or metal closure), the method comprising: providing a metal packaging liquid jet or aerosol jet coating composition of any of Embodiments A; directing the liquid jet or aerosol jet coating composition to at least a portion of the metal substrate; and providing conditions effective for the liquid jet or aerosol jet coating composition to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate.

Embodiment B-2 is a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can), portion thereof, or metal closure), the method comprising: providing a metal substrate; providing a metal packaging liquid jet or aerosol jet coating composition of any of Embodiments A; selectively applying the liquid jet or aerosol jet coating composition on at least a portion of the metal substrate to form a patterned coating; and providing conditions effective for the liquid jet or aerosol jet coating composition to form a hardened adherent patterned coating on at least a portion of the metal substrate.

Embodiment B-3 is a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can), portion thereof, or metal closure), the method comprising: providing a metal substrate; providing multiple metal packaging liquid jet or aerosol jet coating compositions of any of Embodiments A, wherein at least two of the multiple metal packaging liquid jet or aerosol jet

coating compositions are different; directing each of the multiple coating compositions to at least a portion of the metal substrate such that at least one coating composition is deposited on another different coating composition (either prior to or after hardening of the underlying coating composition to form a coating); and providing conditions effective for the multiple liquid jet or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate.

Embodiment B-4 is the method of any of the preceding Embodiments B, wherein providing conditions effective for the liquid jet or aerosol jet coating compositions to form a hardened coating on at least a portion of the metal substrate comprises applying thermal energy (e.g., using a convection oven or induction coil), UV radiation, IR radiation, or electron beam radiation to the liquid jet or aerosol jet coating compositions.

Embodiment B-5 is the method of embodiment B-4, wherein providing conditions comprises applying thermal energy.

Embodiment B-6 is the method of embodiment B-5, wherein applying thermal energy comprises applying thermal energy at a temperature of at least 100°C or at least 177°C.

Embodiment B-7 is the method of embodiment B-5 or B-6, wherein applying thermal energy comprises applying thermal energy at a temperature of up to 300°C or up to 250°C.

Embodiment B-8 is the method of any of the preceding Embodiments B, wherein the metal substrate comprises steel, stainless steel, electrogalvanized steel, tin-free steel (TFS), tin-plated steel, electrolytic tin plate (ETP), or aluminum.

Embodiment B-9 is the method of any of the preceding Embodiments B, wherein the metal substrate is a cryogenically cleaned metal substrate.

Embodiment B-10 is the method of any of the preceding Embodiments B, further comprising cryogenically cleaning the metal substrate prior to directing each of the multiple liquid jet or aerosol jet coating compositions to at least a portion of the metal substrate.

Embodiment B-11 is the method of any of the preceding Embodiments B, wherein the metal substrate has an average thickness of up to 635 microns (or up to 375 microns).

Embodiment B-12 is the method of any of the preceding Embodiments B, wherein the metal substrate has an average thickness of at least 125 microns.

Embodiment B-13 is the method of any of the preceding Embodiments B, wherein the hardened adherent coating has an average total thickness of up to 100 microns, or a maximum thickness up to 100 microns.

Embodiment B-14 is the method of Embodiment B-13, wherein the hardened adherent coating has an average total thickness of up to 50 microns, preferably up to 25 microns (e.g., up to 20 microns, up to 15 microns, up to 10 microns, or up to 5 microns).

Embodiment B-15 is the method of any of the preceding Embodiments B, wherein the hardened adherent coating has an average total thickness of at least 1 micron (or at least 2 microns, at least 3 microns, or at least 4 microns).

Embodiment B-16 is a coated metal substrate having a surface at least partially coated with a coating prepared by the method of any of the preceding Embodiments B.

Embodiment B-17 is the coated metal substrate of Embodiment B-16, wherein the substrate is a drawn and redrawn substrate.

Embodiment B-18 is the coated metal substrate of Embodiment B-16, wherein the metal substrate is tab stock.

Embodiment B-19 is the coated metal substrate of Embodiment B-16, wherein the metal substrate is aluminum coil for making beverage can ends (with the hardened coating applied to an interior or exterior surface of the beverage can end, or both).

Embodiment B-20 is the method of any of the preceding Embodiments B, wherein the liquid jet or aerosol jet coating composition is applied to at least a portion of the metal substrate via a plurality of liquid jetting nozzles distributed evenly across a surface of a cylindrical print head.

Embodiments C: Metal Packaging and Methods of Making

Embodiment C-1 is metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, metal closure, or pull tab for an easy open end) comprising a metal substrate having a surface at least partially coated with a coating prepared by the method of any of Embodiments B-1 through B-15.

Embodiment C-2 is the metal packaging of Embodiment C-1, wherein the surface is an interior surface, an exterior surface, or both, of a container (e.g., can or cup) body.

Embodiment C-3 is the metal packaging of Embodiment C-1 or C-2, wherein the surface is a surface of a riveted can end and/or a pull tab.

Embodiment C-4 is the metal packaging of any of Embodiments C-1 through C-3, which is filled with a food, beverage, or aerosol product.

Embodiment C-5 is a method of making metal packaging (e.g., a metal packaging container such as a food, beverage, aerosol, or general packaging container (e.g., can or cup), a portion thereof, or a metal closure for a container such as a metal can or glass jar)

comprising: providing a metal substrate (e.g., coil or sheet) having a hardened, preferably continuous, adherent coating disposed on at least a portion of a surface thereof as described in Embodiments B-16 through B-19; and forming the substrate (e.g., by stamping) into at least a portion of a metal packaging container (e.g., food, beverage, aerosol, or general packaging can) or a portion thereof, or a metal closure for a container (e.g., metal can or glass jar).

Embodiment C-6 is a method of making metal packaging (e.g., a metal packaging container such as a food, beverage, aerosol, or general packaging container (e.g., can or cup), a portion thereof, or a metal closure such as for a metal packaging container or a glass jar) in one location and/or in one continuous manufacturing line or process, the method comprising: providing a metal substrate; providing a metal packaging liquid jet or aerosol jet coating composition of any of Embodiments A; directing the liquid jet or aerosol jet coating composition to at least a portion of the metal substrate; providing conditions effective for the coating composition to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate; and forming the at least partially coated metal substrate into at least a portion of a metal packaging container (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup)), a portion thereof, or a metal closure (e.g., for a metal packaging container or a glass jar).

Embodiments D: Multilayer Coating Methods and Systems

Embodiment D-1 is a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, or metal closure, or pull tab for an easy open end), the method comprising: providing a metal substrate; providing multiple metal packaging liquid or aerosol jet coating compositions, wherein each liquid or aerosol jet coating composition comprises polymer particles, and at least two of the multiple liquid or aerosol jet coating compositions are different; directing each of the multiple liquid or aerosol jet coating compositions to at least a portion of the metal substrate such that at least one liquid or aerosol jet coating composition is deposited on another different liquid or aerosol jet coating composition (prior to or after at least hardening the one or more different underlying liquid or aerosol jet coating composition); and providing conditions effective for the multiple liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating on at least a portion of the metal substrate; wherein each liquid or aerosol jet coating composition comprises: polymer particles comprising a polymer having a number average

molecular weight of at least 2000 Daltons, wherein the polymer particles have a particle size distribution having a D50 of less than 10 microns.

Embodiment D-2 is the method of Embodiment D-1, wherein providing conditions effective comprises providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating between depositing layers of different liquid or aerosol jet coating compositions (e.g., by heating each respectively deposited layer).

Embodiment D-3 is the method of Embodiment D-1, wherein providing conditions effective comprises providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating after depositing all the layers of different liquid or aerosol jet coating compositions.

Embodiment D-4 is the method of any of the preceding Embodiments D, wherein the different liquid or aerosol jet coating compositions are chemically different.

Embodiment D-5 is the method of Embodiment D-4, wherein the different liquid or aerosol jet coating compositions are in different colors, and the method results in color-on-color printing.

Embodiment D-6 is the method of Embodiment D-5, wherein the liquid or aerosol jet coating composition deposited as the outermost (i.e., top) coating forms a clear coating.

Embodiment D-7 is the method of any of the preceding Embodiments D, wherein the different liquid or aerosol jet coating compositions provide different functions.

Embodiment D-8 is the method of Embodiment D-7, wherein a first liquid or aerosol jet coating composition is deposited to provide a relatively soft, flexible primer layer, and a second liquid or aerosol jet coating composition is deposited on the first liquid or aerosol jet coating composition to provide a relatively hard, abrasion-resistant top coating.

Embodiment D-9 is the method of any of the preceding Embodiments D, wherein the different liquid or aerosol jet coating compositions are deposited in different amounts to form coating layers having different thicknesses.

Embodiment D-10 is the method of any of the preceding Embodiments D, wherein the multiple liquid or aerosol jet coating compositions are deposited in a manner to form a textured surface.

Embodiment D-11 is the method of any of Embodiments D-1 through D-9, wherein the multiple liquid or aerosol jet coating compositions are deposited in a manner to form a smooth surface.

Embodiment D-12 is the method of any of the preceding Embodiments D, wherein the hardened, preferably continuous, adherent coating forms markings.

Embodiment D-13 is the method of any of the preceding Embodiments D, wherein the metal substrate is a cryogenically cleaned metal substrate.

5 Embodiment D-14 is the method of any of the preceding Embodiments D, further comprising cryogenically cleaning the metal substrate prior to directing each of the multiple liquid or aerosol jet coating compositions to at least a portion of the metal substrate.

Embodiment D-15 is the method of any of the preceding Embodiments D, wherein the metal substrate has an average thickness of up to 635 microns (or up to 375 microns).

10 Embodiment D-16 is the method of any of the preceding Embodiments D, wherein the metal substrate has an average thickness of at least 125 microns.

Embodiment D-17 is the method of any of the preceding Embodiments D, wherein the hardened adherent coating has an average total thickness of up to 100 microns, or a maximum thickness up to 100 microns.

15 Embodiment D-18 is the method of Embodiment D-17, wherein the hardened adherent coating has an average total thickness of up to 50 microns, preferably up to 25 microns (e.g., up to 20 microns, up to 15 microns, up to 10 microns, or up to 5 microns).

Embodiment D-19 is the method of any of the preceding Embodiments D, wherein the hardened adherent coating has an average total thickness, or a minimum thickness, of at least
20 1 micron (or at least 2 microns, at least 3 microns, or at least 4 microns).

Embodiment D-20 is the method of any of the preceding Embodiments D, wherein one or more of the multiple liquid or aerosol jet coating compositions comprise polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons (or at least 5,000 Daltons, at least 10,000 Daltons, or at least 15,000 Daltons).

25 Embodiment D-21 is the method of any of the preceding Embodiments D, wherein one or more of the multiple liquid or aerosol jet coating compositions comprise polymer particles comprising a polymer having a number average molecular weight of up to 10,000,000 Daltons (or up to 1,000,000 Daltons, up to 100,000 Daltons, or up to 20,00 Daltons).

30 Embodiment D-22 is the method of any of the preceding Embodiments D, wherein one or more of the multiple liquid or aerosol jet coating compositions comprise polymer particles comprising a polymer having a polydispersity index (M_w/M_n) of less than 4 (or less than 3, less than 2, or less than 1.5).

Embodiment D-23 is the method of any of Embodiments D-20 through D-22, wherein one or more of the multiple liquid or aerosol jet coating compositions comprise the polymer in an amount of at least 40 wt-%, at least 50 wt-%, at least 60 wt-%, at least 70 wt-%, at least 80 wt-%, at least 90 wt-%, or at least 95 wt-%.

5 Embodiment D-24 is the method of any of the preceding Embodiments D, wherein one or more of the multiple liquid or aerosol jet coating compositions comprise polymer particles having a particle size distribution having a D50 of less than 5 microns (or less than 1 micron, or less than 0.5 micron).

10 Embodiment D-25 is the method of any of the preceding Embodiments D, wherein one or more of the multiple liquid or aerosol jet coating compositions comprise polymer particles having a particle size distribution having a D90 of less than 5 microns (or less than 1 micron, or less than 0.5 micron).

15 Embodiment D-26 is a packaging coating system, comprising: multiple metal packaging liquid or aerosol jet coating compositions, wherein at least two of the multiple metal packaging liquid or aerosol jet coating compositions are different; wherein each liquid or aerosol jet coating composition comprises polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons, wherein the polymer particles have a particle size distribution having a D50 of less than 10 microns.

20 Embodiment D-27 is the system of Embodiment D-26, further comprising instructions comprising: directing each of the multiple liquid or aerosol jet coating compositions to at least a portion of a metal substrate such that at least one liquid or aerosol jet coating composition is deposited on another different liquid or aerosol jet coating composition; and providing conditions effective for the multiple liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating on at least a portion of the metal
25 substrate.

Embodiment D-28 is the system of Embodiment D-26 and D-27, wherein at least two of the metal packaging liquid or aerosol jet coating compositions differ in one or more chemical or physical properties.

30 Embodiment D-29 is the system of Embodiment D-28, wherein the properties include polymer particle properties (such as molecular weight, density, glass transition temperature (T_g), melting temperature (T_m), intrinsic viscosity (IV), melt viscosity (MV), melt index (MI), crystallinity, arrangement of blocks or segments, availability of reactive sites, reactivity, acid number), and coating composition properties (such as surface energy, hydrophobicity, oleophobicity, moisture or oxygen permeability, transparency, heat

resistance, resistance to sunlight or ultraviolet energy, adhesion to metals, color or other visual effects, and recyclability).

Embodiment D-30 is the system of Embodiment D-28 or D-29, wherein a particular property of at least two different liquid or aerosol jet coating compositions differ by at least

5 $\pm 5\%$, at least $\pm 10\%$, at least $\pm 15\%$, at least $\pm 25\%$, at least $\pm 50\%$, at least $\pm 100\%$, or more.

Embodiments E: Patterned Coating Methods, Systems, and Resultant Products

Embodiment E-1 is a method of coating a metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, metal closure, or pull tab for an easy open end), the method comprising:

10 providing a metal substrate; providing a metal packaging liquid or aerosol jet coating composition, wherein the liquid or aerosol jet coating composition comprises polymer particles; selectively applying the liquid or aerosol jet coating composition on at least a portion of the metal substrate to form a patterned coating; and providing conditions effective for the liquid or aerosol jet coating composition to form a hardened adherent patterned
15 coating (which may or may not be continuous) on at least a portion of the metal substrate.

Embodiment E-2 is the method of Embodiment E-1, wherein the hardened adherent patterned coating forms markings.

Embodiment E-3 is the method of Embodiment E-1, wherein the hardened adherent patterned coating is in the form of a ring-shaped coating on a metal substrate.

20 Embodiment E-4 is the method of embodiment E-3, wherein the ring-shaped coating is a top coat localized in a metal closure to contact a PVC gasket.

Embodiment E-5 is the method of embodiment E-1, wherein the hardened adherent patterned coating is in the form of a spot coating on a food or beverage can end.

25 Embodiment E-6 is the method of embodiment E-5, wherein the hardened adherent patterned coating is in the form of a spot coating on a product-contact area of a food or beverage can end.

Embodiment E-7 is the method of any of the preceding Embodiments E, wherein the liquid or aerosol jet coating composition is intentionally and selectively deposited in different amounts to form a coating having different thicknesses across the coated surface.

30 Embodiment E-8 is the method of the preceding Embodiments E, further comprising directing a different liquid or aerosol jet coating composition to at least a portion of the metal substrate to form a hardened, preferably continuous, adherent coating, which may be a patterned coating or an all-over coating, before or after forming the patterned coating. In

certain embodiments of the preceding Embodiments E, the method further comprises applying a conventional liquid coating to the metal substrate to form an all-over coating before forming the patterned coating.

Embodiment E-9 is the method of any of the preceding Embodiments E, wherein:

5 providing a metal packaging liquid or aerosol jet coating composition comprises providing multiple metal packaging liquid or aerosol jet coating compositions, wherein each liquid or aerosol jet coating composition comprises polymer particles, and at least two of the multiple metal packaging liquid or aerosol jet coating compositions are different; directing the liquid or aerosol jet coating composition comprises directing each of the multiple liquid or aerosol
10 jet coating compositions to at least a portion of the metal substrate such that at least one liquid or aerosol jet coating composition is optionally deposited on another different liquid or aerosol jet coating composition to form a coating; and providing conditions comprise providing conditions effective for each of the multiple liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating.

15 Embodiment E-10 is the method of Embodiment E-8 or C-9, wherein providing conditions comprise providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating between depositing layers of different liquid or aerosol jet coating compositions.

Embodiment E-11 is the method of Embodiment E-8 or C-9, wherein providing
20 conditions effective comprises providing conditions effective for each of the liquid or aerosol jet coating compositions to form a hardened, preferably continuous, adherent coating after depositing all the layers of different liquid or aerosol jet coating compositions.

Embodiment E-12 is the method of any of Embodiments E-8 through E-11, wherein the different liquid or aerosol jet coating compositions are chemically different.

25 Embodiment E-13 is the method of Embodiment E-12, wherein the different liquid or aerosol jet coating compositions are in different colors, and the method results in color-on-color printing.

Embodiment E-14 is the method of Embodiment E-13, wherein the liquid or aerosol jet coating composition deposited as the outermost (i.e., top) coating forms a clear coating.

30 Embodiment E-15 is the method of any of Embodiments E-8 through C-14, wherein the different liquid or aerosol jet coating compositions provide different functions.

Embodiment E-16 is the method of Embodiment E-15, wherein a first liquid or aerosol jet coating composition is deposited to provide a relatively soft, flexible, primer layer,

and a second liquid or aerosol jet coating composition is deposited on the first liquid or aerosol jet coating composition to provide a relatively hard, abrasion-resistant top coating.

Embodiment E-17 is the method of any of Embodiments E-8 through E-16, wherein the different liquid or aerosol jet coating compositions are deposited in different amounts to
5 form coating layers having different thicknesses.

Embodiment E-18 is the method of any of the preceding Embodiments E, wherein the one or more liquid or aerosol jet coating compositions are deposited in a manner to form a textured surface, or in a manner to form a smooth surface.

Embodiment E-19 is the method of any of the preceding Embodiments E, wherein the
10 one or more liquid or aerosol jet coating compositions are deposited in a manner to form a gradient pattern.

Embodiment E-20 is the method of any of the preceding Embodiments E, wherein the metal substrate is a cryogenically cleaned metal substrate.

Embodiment E-21 is the method of any of the preceding Embodiments E, further
15 comprising cryogenically cleaning the metal substrate prior to directing each of the liquid or aerosol jet coating composition(s) to at least a portion of the metal substrate.

Embodiment E-22 is the method of any of the preceding Embodiments E, wherein the metal substrate has an average thickness of up to 635 microns (or up to 375 microns).

Embodiment E-23 is the method of any of the preceding Embodiments E, wherein the
20 metal substrate has an average thickness of at least 125 microns.

Embodiment E-24 is the method of any of the preceding Embodiments E, wherein the hardened adherent patterned coating has an average total thickness of up to 100 microns, or a maximum total thickness up to 100 microns.

Embodiment E-25 is the method of Embodiment E-24, wherein the hardened adherent
25 patterned coating has an average total thickness of up to 50 microns, preferably up to 25 microns (e.g., up to 20 microns, up to 15 microns, up to 10 microns, or up to 5 microns).

Embodiment E-26 is the method of any of the preceding Embodiments E, wherein the hardened adherent patterned coating has an average total thickness, or a minimum thickness, of at least 1 micron (or at least 2 microns, at least 3 microns, or at least 4 microns).

Embodiment E-27 is the method of any of the preceding Embodiments E, wherein one
30 or more of the liquid or aerosol jet coating compositions comprise polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons (or at least 5,000 Daltons, at least 10,000 Daltons, or at least 15,000 Daltons).

Embodiment E-28 is the method of any of the preceding Embodiments E, wherein one or more of the liquid or aerosol jet coating compositions comprise polymer particles comprising a polymer having a number average molecular weight of up to 10,000,000 Daltons (or up to 1,000,000 Daltons, up to 100,000 Daltons, or up to 20,00 Daltons).

5 Embodiment E-29 is the method of any of the preceding Embodiments E, wherein one or more of the liquid or aerosol jet coating compositions comprise polymer particles comprising a polymer having a polydispersity index (M_w/M_n) of less than 4 (or less than 3, less than 2, or less than 1.5).

10 Embodiment E-30 is the method of any of the preceding Embodiments E, wherein one or more of the liquid or aerosol jet coating compositions comprise polymer particles having a particle size distribution having a D50 of less than 10 microns (or less than 5 microns, less than 1 micron, or less than 0.5 micron), or a D90 of less than 10 microns (or less than 5 microns, less than 1 micron, or less than 0.5 micron).

15 Embodiment E-31 is a pattern-coated metal substrate suitable for use in forming metal packaging (e.g., a food, beverage, aerosol, or general packaging container (e.g., can or cup), portion thereof, metal closure, or pull tab for an easy open end), wherein at least a portion of the metal substrate has a surface coated with a hardened adherent patterned coating prepared according to any of the preceding Embodiments E.

20 Embodiment E-32 is metal packaging (e.g., a metal packaging container such as a food, beverage, aerosol, or general packaging container (e.g., can or cup), a portion thereof, a metal closure, or pull tab) comprising a metal substrate having a surface at least partially coated with a coating prepared by the method of any of Embodiments E-1 through E-30.

25 Embodiment E-33 is a packaging coating system for patterned coating, comprising: one or more metal packaging liquid or aerosol jet coating compositions; wherein each liquid or aerosol jet coating composition comprises polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons, wherein the polymer particles have a particle size distribution having a D50 of less than 10 microns; and instructions comprising: directing the one or more liquid or aerosol jet coating compositions to at least a portion of the metal substrate to form a patterned coating; and providing conditions effective
30 for the one or more liquid or aerosol jet coating compositions to form a hardened adherent patterned coating (which may or may not be continuous) on at least a portion of the metal substrate.

Embodiment E-34 is the system of Embodiment E-33 comprising at least two different metal packaging liquid or aerosol jet coating compositions that differ in one or more chemical or physical properties.

Embodiment E-35 is the system of Embodiment E-34, wherein the properties include
5 polymer particle properties (such as molecular weight, density, glass transition temperature (T_g), melting temperature (T_m), intrinsic viscosity (IV), melt viscosity (MV), melt index (MI), crystallinity, arrangement of blocks or segments, availability of reactive sites, reactivity, acid number), and coating composition properties (such as surface energy, hydrophobicity, oleophobicity, moisture or oxygen permeability, transparency, heat
10 resistance, resistance to sunlight or ultraviolet energy, adhesion to metals, color or other visual effects, and recyclability).

TEST METHODS

Unless indicated otherwise, the following test methods may be utilized.

Adhesion Test

15 Adhesion testing was performed according to ASTM D 3359-17 (2017), Test Method B, for coatings $\leq$ 125 microns thick, using SCOTCH 610 tape (available from 3M Company of Saint Paul, MN) and a lattice pattern consisting of 4 scratches across and 4 scratches down (roughly 1-2 mm apart). The test is typically repeated 3 times per sample. Adhesion is rated on a scale of 0-10 where a rating of “10” indicates no adhesion failure, a
20 rating of “9” indicates 90% of the coating remains adhered, a rating of “8” indicates 80% of the coating remains adhered, and so on. Adhesion ratings of 9 or 10 are typically desired for commercially viable coatings. Thus, herein, an adhesion rating of 9 or 10, preferably 10, is considered to be adherent.

Differential Scanning Calorimetry for T_g

25 Samples of the overall hardened coating for differential scanning calorimetry (“DSC”) testing are weighed into standard sample pans, and analyzed using the standard DSC heat-cool-heat method. The samples are equilibrated at -60°C, then heated at 20°C per minute to 200°C, cooled to -60°C, and then heated again at 20°C per minute to 200°C. Glass transition temperatures are calculated from the thermogram of the last heat cycle. The glass transition
30 is measured at the inflection point of the transition.

Molecular Weight Determination by Gel Permeation Chromatography

Samples for Gel Permeation Chromatography (“GPC”) testing are prepared by first dissolving the overall hardened coating in a suitable solvent (e.g., THF if appropriate for a given overall hardened coating). An aliquot of this solution is then analyzed by GPC along
5 with mixtures of polystyrene (“PS”) standards. The molecular weights of the samples are calculated after processing the GPC runs and verifying the standards.

Global Extraction Test

The global extraction test is designed to estimate the total amount of mobile material that can potentially migrate out of a coating and into food packed in a coated can. Typically,
10 a coated substrate is subjected to water or solvent blends under a variety of conditions to simulate a given end-use.

Acceptable extraction conditions and media can be found in 21 CFR §175.300, paragraphs (d) and (e). The extraction procedure used in the current disclosure was conducted in accordance with the Food and Drug Administration (FDA) “Preparation of Premarket
15 Submission for Food Contact Substances: Chemistry Recommendations,” (December 2007). The allowable global extraction limit as defined by the FDA regulation is 50 parts per million (ppm).

The single-sided extraction cells are made according to the design found in the Journal of the Association of Official Analytical Chemists, 47(2):387(1964), with minor
20 modifications. The cell is 9 in (inches) x 9 in x 0.5 in with a 6 in x 6 in open area in the center of the TEFLON spacer. This allows for 36 in² or 72 in² of test article to be exposed to the food simulating solvent. The cell holds 300 mL of food simulating solvent. The ratio of solvent to surface area is then 8.33 mL/in² and 4.16 mL/in² when 36 in² and 72 in² respectively of test article are exposed.

For the purpose of this disclosure, the test articles consist of 0.0082-inch-thick 5182
25 aluminum alloy panels, pretreated with PERMATREAT® 1903 (supplied by Chemetall GmbH, Frankfurt am Main, Germany). These panels are coated with the test coating (completely covering at least the 6 in x 6 in area required to fit the test cell) to yield a final, dry film thickness of 11 grams per square meter (gsm) following a 10 second curative bake
30 resulting in a 242°C peak metal temperature (PMT). Two test articles are used per cell for a total surface area of 72 in² per cell. The test articles are extracted in quadruplicate using 10% aqueous ethanol as the food-simulating solvent. The test articles are processed at 121°C for two hours, and then stored at 40°C for 238 hours. The test solutions are sampled after 2, 24,

96 and 240 hours. The test article is extracted in quadruplicate using the 10% aqueous ethanol under the conditions listed above.

Each test solution is evaporated to dryness in a preweighed 50 mL beaker by heating on a hot plate. Each beaker is dried in a 250°F (121°C) oven for a minimum of 30 minutes.

- 5 The beakers are then placed into a desiccator to cool and then weighed to a constant weight. Constant weight is defined as three successive weighings that differ by no more than 0.00005 g.

Solvent blanks using Teflon sheet in extraction cells are similarly exposed to simulant and evaporated to constant weight to correct the test article extractive residue weights for extractive residue added by the solvent itself. Two solvent blanks are extracted at each time
10 point and the average weight is used for correction.

Total nonvolatile extractives are calculated as follows:

$$E_x = \frac{e}{s}$$

where: E_x = Extractive residues (mg/in²)

15 e = Extractives per replicate tested (mg)

s = Area extracted (in²)

Preferred coatings give global extraction results of less than 50 ppm, more preferred results of less than 10 ppm, even more preferred results of less than 1 ppm. Most preferably,
20 the global extraction results are optimally non-detectable.

Flat Panel Continuity Test

This test measures the continuity of a coating applied to a flat metal substrate and indicates the presence or absence of a continuous film, largely free of pores, cracks, or other defects that could expose the metal substrate. This method may be used for both laboratory
25 and commercially coated steel and aluminum substrates. A test assembly is employed that consists of: a non-conducting, solid base (large enough to support the test panel); a hinged clamping mechanism that is mounted to the base; a non-conductive electrolyte holding cell, connected to the clamping mechanism in such a way that it can be lowered and sealed onto the test panel (resulting in a 6 inch-diameter, circular area on the test panel being exposed to
30 the electrolyte); a hole in the electrolyte holding cell large enough to fill the cell with electrolyte; and an electrode inserted into the electrolyte holding cell. A WACO Enamel Rater II (available from the Wilkens-Anderson Company, Chicago, IL), with an output

voltage of 6.3 volts is used in conjunction with the test assembly (as described below) to measure metal exposure in the form of electrical current. The electrolyte solution used in the following test consists of 1%-by-weight Sodium Chloride dissolved in deionized water.

5 An 8-inch by 8-inch panel of metal is coated and cured with the coating to be tested, as prescribed by the formula or technical data sheet. If no coating thickness or cure schedule is prescribed for the test coating, test panels should be coated in such a way to yield a final, dry film thickness of 11 grams per square meter (gsm) utilizing a curative bake with an appropriate duration to achieve a 242°C peak metal temperature (PMT). Each test panel may only be used once and should be visibly free of scratches or abrasions. The test panel is
10 placed in the test assembly with the test coating facing up. The electrolyte holding cell is then lowered onto the test panel and locked in place by closing the clamp. The positive lead wire from the enamel rater is connected to the edge of the panel in an area free of coating. A small area may need to be sanded or scraped to expose the bare metal substrate. The electrolyte cell is then filled with enough electrolyte solution to ensure contact with the cell's
15 negative post. The negative lead wire from the enamel rater is connected to the negative post on top of the cell. Finally, the probe on the Waco enamel rater is lowered to activate the test current.

Film imperfections/failure will be indicated by a current flow measured in milliamps (mA). The initial milliamp reading is recorded for each panel tested, and results are reported
20 in milliamps. If more than one determination per variable is run, the average reading is reported.

For purposes of this application, a continuous coating passes less than 200 mA when evaluated according to this test. Preferred coatings of the present disclosure pass less than 100 milliamps (mA), more preferably less than 50 mA, less than 10 mA, or less than 5 mA,
25 most preferably less than 2 mA, and optimally less than 1 mA, according to this test.

Flexibility Test

This test measures the ability of a coated substrate to retain its integrity as it undergoes the formation process necessary to produce a fabricated article such as a riveted beverage can end. It is a measure of the presence or absence of cracks or fractures in the
30 formed end. The end is typically placed on a cup filled with an electrolyte solution. The cup is inverted to expose the surface of the end to the electrolyte solution. The intensity of the current that passes through the end is then measured. If the coating remains intact (no cracks or fractures) after fabrication, minimal current will pass through the end.

For the present evaluation, fully converted 202 standard opening beverage ends were exposed for a period of 4 seconds to a room-temperature electrolyte solution comprised of 1% NaCl by weight in deionized water. The coating to be evaluated was present on the interior surface of the beverage end at a dry film thickness of 6 to 7.5 milligrams per square inch (“msi”) (or 9.3 to 11.6 grams per square meter), with 7 msi being the target thickness and having been cured as prescribed by the formula or technical data sheet. If no cure schedule is prescribed for the test coating, test panels should be coated utilizing a curative bake with an appropriate duration to achieve a 242°C peak metal temperature (PMT). Metal exposure was measured using a WACO Enamel Rater II (available from the Wilkens-Anderson Company, Chicago, IL) with an output voltage of 6.3 volts. The measured electrical current intensity, in milliamps, is reported. End continuities are typically tested initially and then after the ends are subjected to pasteurization, Dowfax, or retort.

Coatings of the present disclosure initially “pass” this test if they pass less than 200 milliamps (mA) of current. Preferred coatings of the present disclosure initially pass less than 100 milliamps (mA), more preferably less than 50 mA, less than 10 mA, or less than 5 mA, most preferably less than 2 mA, and optimally less than 1 mA, according to this test.

After pasteurization, Dowfax detergent test, or retort, preferred coatings give continuities of less than 20 mA, more preferably less than 10 mA, even more preferably less than 5 mA, and even more preferably less than 1 mA.

Fabrication Test

This test measures the ability of a coated substrate to retain its integrity as it undergoes the formation process necessary to produce a fabricated article such as a beverage can end. It is a measure of the presence or absence of cracks or fractures in the formed end. The end is typically placed on a cup filled with an electrolyte solution. The cup is inverted to expose the surface of the end to the electrolyte solution. The amount of electrical current that passes through the end is then measured. If the coating remains intact (no cracks or fractures) after fabrication, minimal current will pass through the end. For the present evaluation, fully converted 202 standard opening beverage ends were exposed for a period of 4 seconds to a room-temperature electrolyte solution comprised of 1% NaCl by weight in deionized water. The coating to be evaluated was present on the interior surface of the beverage end at a dry film thickness of 6 to 7.5 milligrams per square inch (“msi”) (or 9.3 to 11.6 grams per square meter), with 7 msi being the target thickness. Metal exposure was measured using a WACO

Enamel Rater II, available from the Wilkens Anderson Company, Chicago, Ill., with an output Voltage of 6.3 volts. The measured electrical current, in milliamps, is reported.

Taber Abrasion Test

This test method uses a Taber Abrader test device (5150 Abrader, Taber Industries, Tonawanda, NY) which has been modified to permit abrasion testing of can coatings which have been applied to 3.25 inch square flat sheets of 0.0082 inch thick aluminum with a 0.25 inch hole drilled through the middle of the sheets. The test involves cyclic abrasion of the test piece using a ¼ inch diameter ball bearing as the abrader. The ball bearing is highly polished and is of approximately the same Rockwell hardness as the dies used to fabricate can ends. Break through to the substrate is determined electrically using a Fluke DMM multimeter (Fluke Corporation, Everett, WA) and Alcoa enamel rater solution. Upon break through to the substrate, the ball bearings surface will be damaged. The ball bearing is therefore used once and then discarded. Results are reported as the number of cycles completed prior to breakthrough (electric continuity) of the test coating.

The complete disclosures of the patents, patent documents, and publications cited herein are incorporated by reference in their entirety as if each were individually incorporated. To the extent that there is any conflict or discrepancy between this specification as written and the disclosure in any document that is incorporated by reference herein, this specification as written will control. Various modifications and alterations to this disclosure will become apparent to those skilled in the art without departing from the scope and spirit of this disclosure. It should be understood that this disclosure is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the disclosure intended to be limited only by the embodiments set forth herein as follows.

WHAT IS CLAIMED IS:

1. A method of coating a coil substrate, the method comprising:
directing a liquid jet or aerosol jet coating composition to at least a portion of the coil substrate, the liquid jet or aerosol jet coating composition comprising:
 - 5 polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons, wherein the polymer particles have a particle size distribution having a D50 of less than 10 microns; and
 - a liquid carrier comprising water in a major amount of the liquid carrier; andproviding conditions effective for the liquid jet or aerosol jet coating composition to
10 form a hardened continuous adherent coating on at least a portion of the coil substrate.
2. A metal packaging liquid jet or aerosol jet coating composition comprising:
polymer particles comprising a polymer having a number average molecular weight of at least 2000 Daltons, wherein the polymer particles have a particle size distribution having a D50 of less than 10 microns; and
15 a liquid carrier comprising water in a major amount of the liquid carrier.
3. A method of coating a metal substrate suitable for use in forming metal packaging, the method comprising:
providing a metal packaging liquid jet or aerosol jet coating composition of claim 1;
directing the liquid jet or aerosol jet coating composition to at least a portion of the
20 metal substrate; and
providing conditions effective for the liquid jet or aerosol jet coating composition to form a hardened continuous adherent coating on at least a portion of the metal substrate.
4. A method of coating a metal substrate suitable for use in forming metal packaging, the method comprising: providing a metal substrate;
25 providing a metal packaging liquid jet or aerosol jet coating composition of claim 1;
selectively applying the liquid jet or aerosol jet coating composition on at least a portion of the metal substrate to form a patterned coating; and
providing conditions effective for the liquid jet or aerosol jet coating composition to form a hardened adherent patterned coating on at least a portion of the metal substrate.
- 30 5. A method of coating a metal substrate suitable for use in forming metal packaging, the method comprising:

providing a metal substrate; providing multiple metal packaging liquid jet or aerosol jet coating compositions of claim 1, wherein at least two of the multiple metal packaging liquid jet or aerosol jet coating compositions are different;

5 directing each of the multiple coating compositions to at least a portion of the metal substrate such that at least one coating composition is deposited on another different coating composition (either prior to or after hardening of the underlying coating composition to form a coating); and

10 providing conditions effective for the multiple liquid jet or aerosol jet coating compositions to form a hardened continuous adherent coating on at least a portion of the metal substrate.

6. A coated metal substrate having a surface at least partially coated with a coating prepared by the method of any of the preceding claims 2 through 4.

7. The coated metal substrate of claim 5, wherein the substrate is a drawn and redrawn substrate.

15 8. The coated metal substrate of claim 5, wherein the metal substrate is tab stock.

9. The coated metal substrate of claim 5, wherein the metal substrate is aluminum coil for making beverage can ends with the hardened coating applied to an interior or exterior surface of the beverage can end, or both.

20 10. Metal packaging comprising a metal substrate having a surface at least partially coated with a coating prepared by the method of any of claims 2 through 4.

11. The metal packaging of claim 9, wherein the surface is an interior surface, an exterior surface, or both, of a container (e.g., can or cup) body.

12. The metal packaging of claim 9 or 10, wherein the surface is a surface of a riveted can end and/or a pull tab.

25 13. The metal packaging of any of claims 9 through 11, which is filled with a food, beverage, or aerosol product.

14. A method of making metal packaging, the method comprising: providing a coated metal substrate of claims 5 through 8; and forming the substrate into at least a portion of a metal packaging container or a portion thereof, or a metal closure for a container.

15. A method of making metal packaging in one location and/or in one continuous manufacturing line or process, the method comprising:

providing a metal substrate;

providing a metal packaging liquid jet or aerosol jet coating composition of claim 1;

directing the liquid jet or aerosol jet coating composition to at least a portion of the metal substrate;

providing conditions effective for the coating composition to form a hardened continuous adherent coating on at least a portion of the metal substrate; and

forming the at least partially coated metal substrate into at least a portion of a metal packaging container, a portion thereof, or a metal closure.

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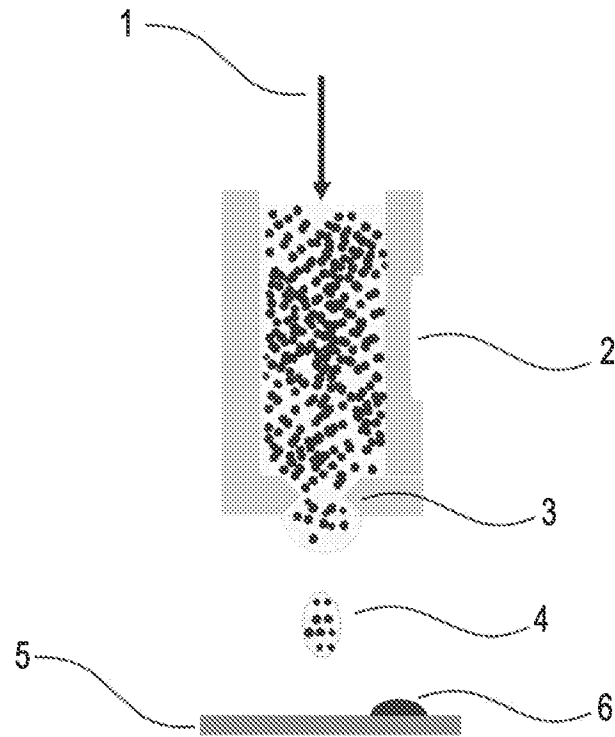


Fig. 1

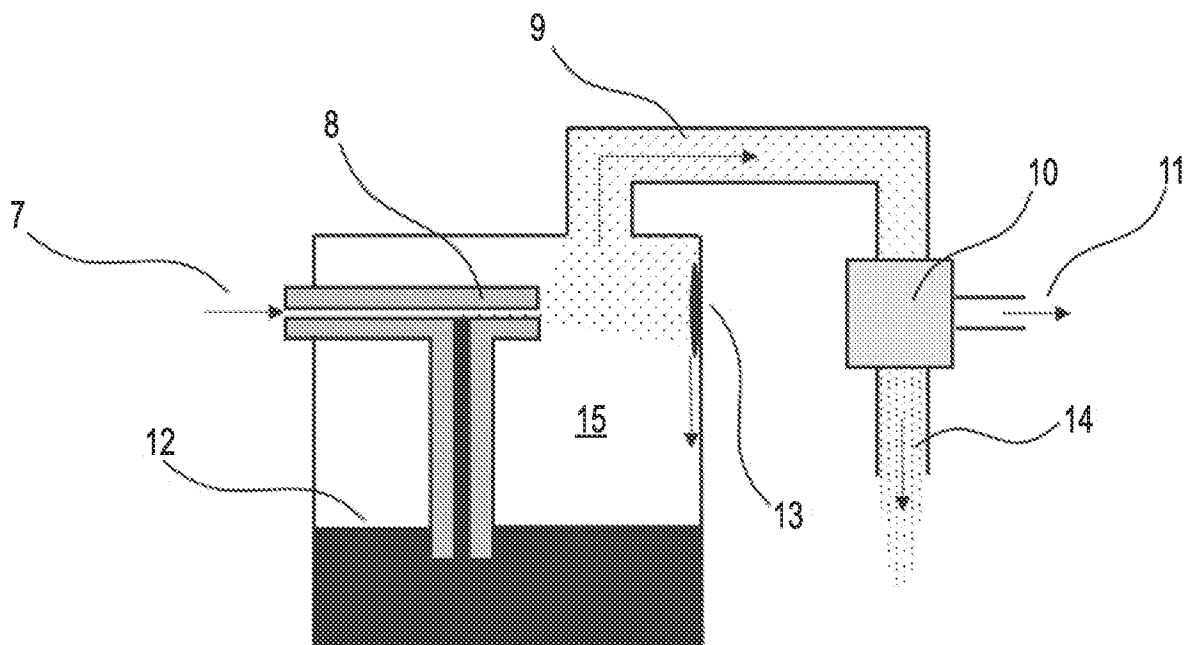
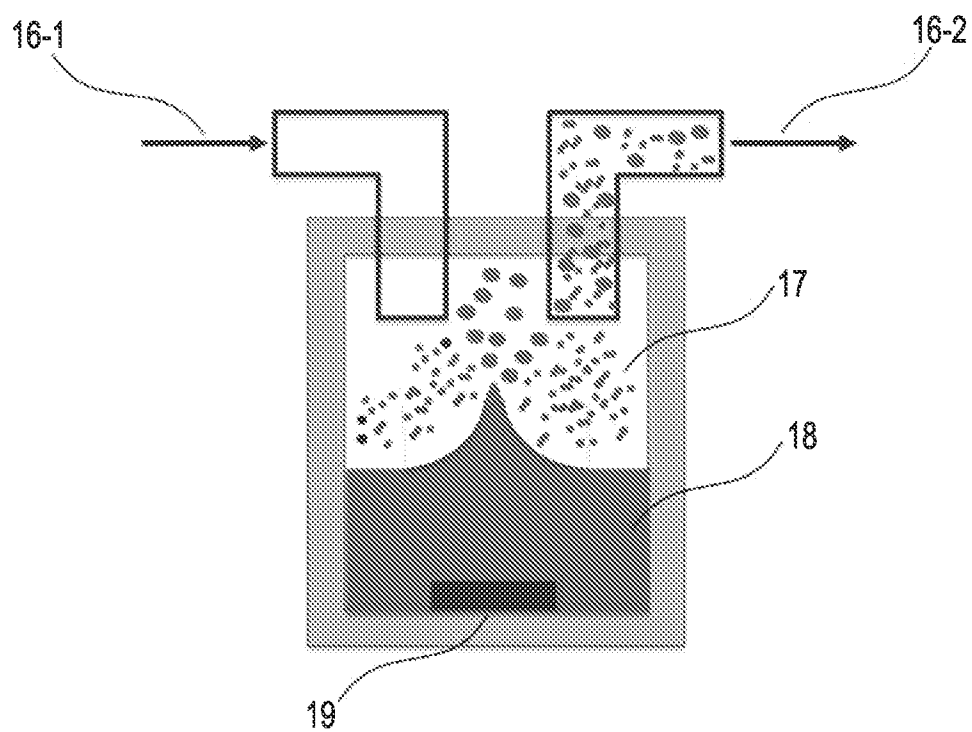
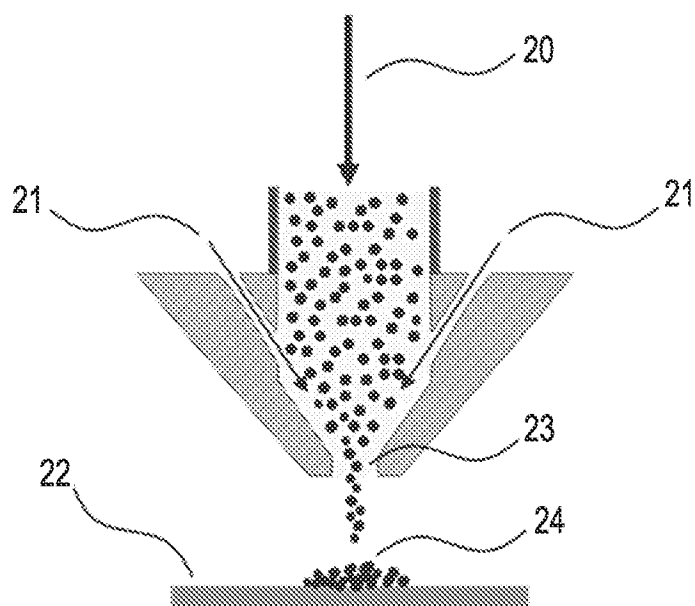
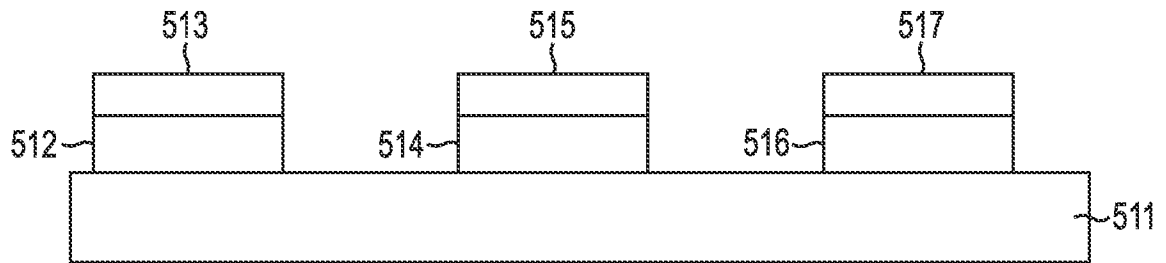
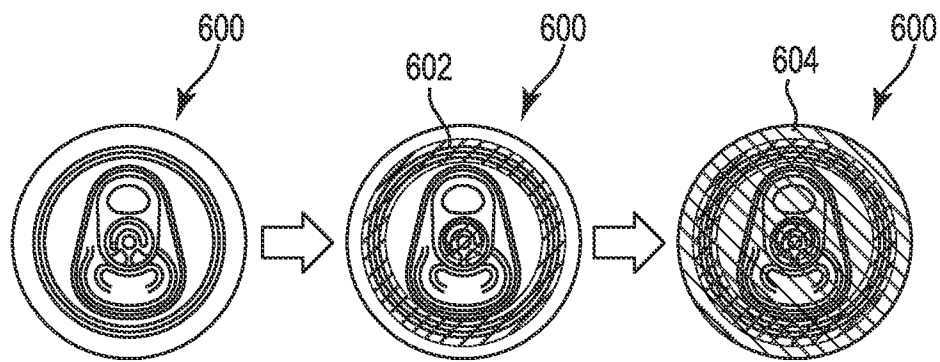


Fig. 2

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**Fig. 3****Fig. 4**

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**Fig. 5****Fig. 6**

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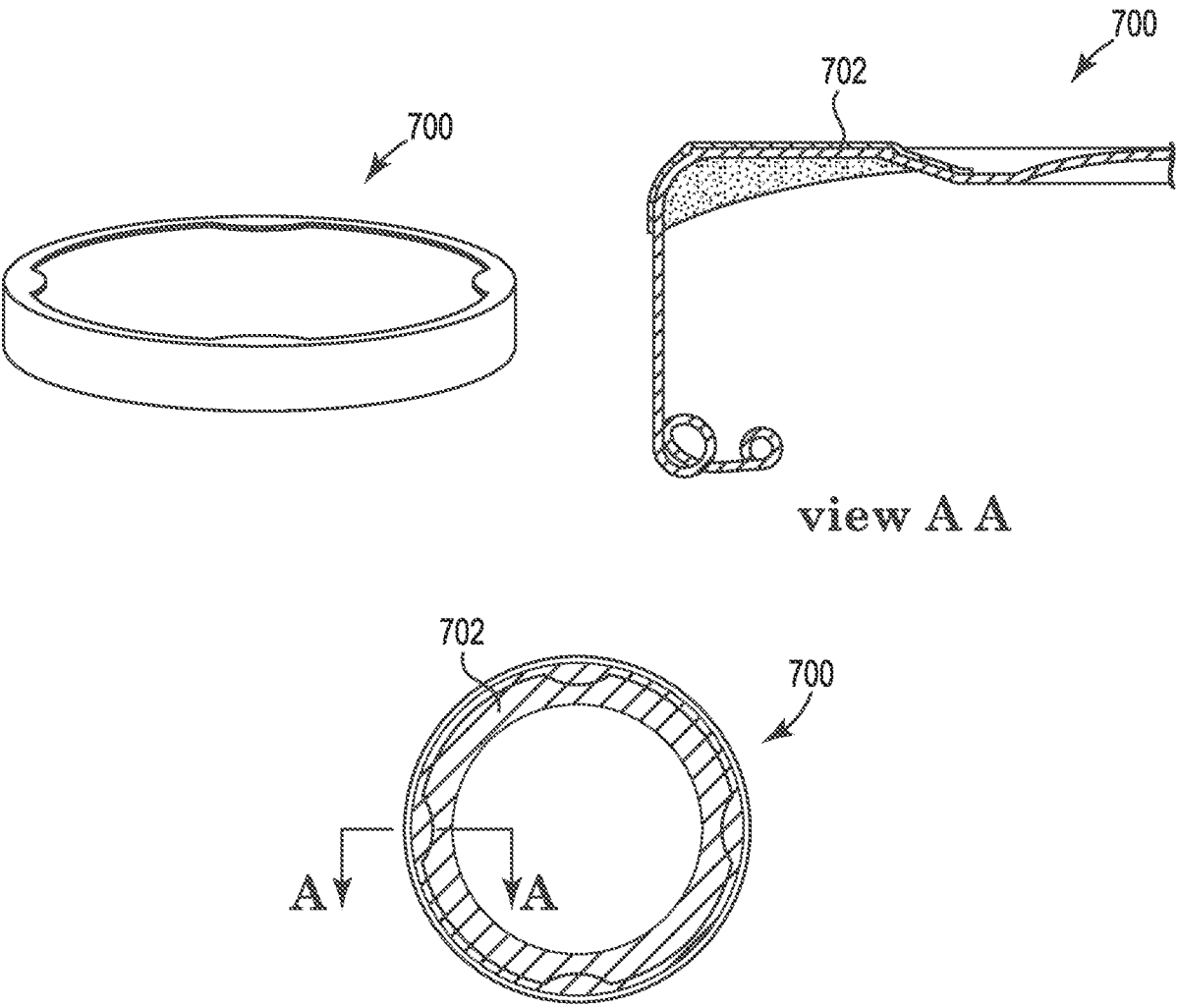


Fig. 7

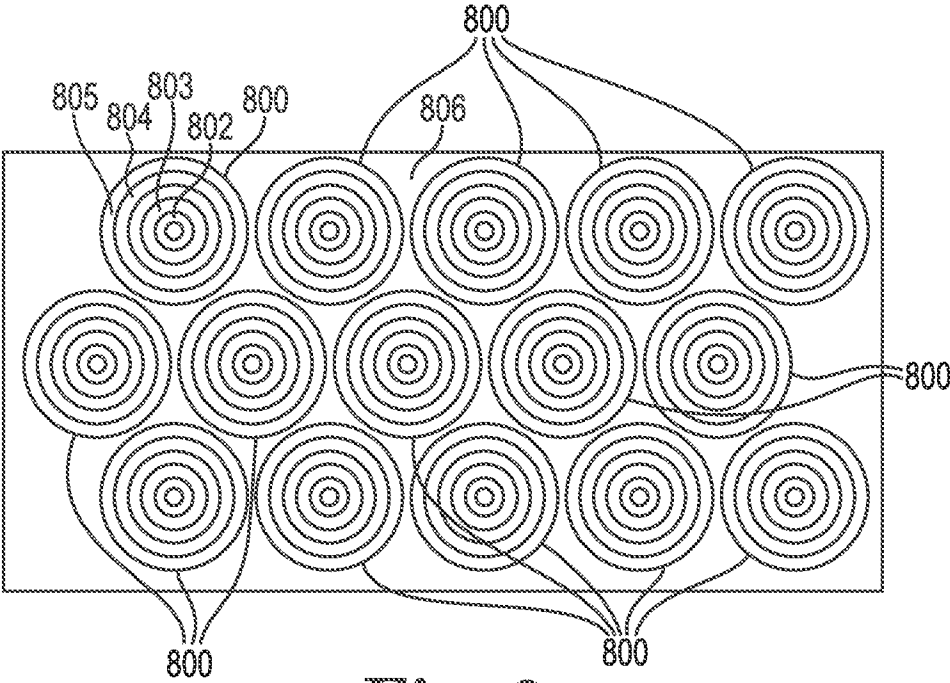
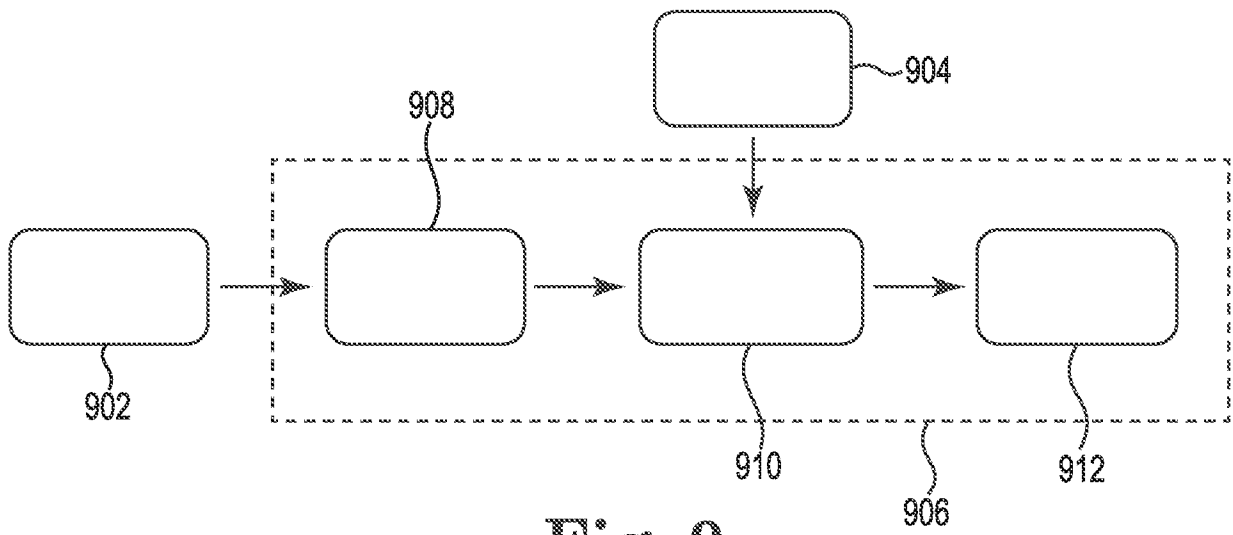


Fig. 8

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**Fig. 9**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2022/030124

A. CLASSIFICATION OF SUBJECT MATTER**C23C 26/00**(2006.01)i; **B65D 85/72**(2006.01)i; **C09K 3/30**(2006.01)i

FI: C23C26/00 A; B65D85/72; C09K3/30 E

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)

C09K3/30; B65D85/72; C23C26/00

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2022
 Registered utility model specifications of Japan 1996-2022
 Published registered utility model applications of Japan 1994-2022

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/0218426 A1 (HONEYWELL INTERNATIONAL INC.) 06 August 2015 (2015-08-06)	2-3,5-15
Y	claim 1, paragraphs [0032], [0034], [0072]	1,3-15
Y	US 2019/0338144 A1 (SWIMC LLC) 07 November 2019 (2019-11-07)	1,3-15
A	paragraphs [0003], [0158], Fig.5	2
Y	JP 2011-213364 A (KOBE STEEL LTD) 27 October 2011 (2011-10-27)	4,6,10,12-14
A	claims 1, 3	1-3,5,7-9,11,15



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
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 “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

20 July 2022

Date of mailing of the international search report

09 August 2022

Name and mailing address of the ISA/JP

Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2022/030124

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2015/0218426	A1	06 August 2015	JP	2017-514935	A	
				EP	3131859	A1	
				KR	10-2016-0146825	A	
				CN	106458755	A	
US	2019/0338144	A1	07 November 2019	EP	3016868	A1	
				CN	105377703	A	
JP	2011-213364	A	27 October 2011	(Family: none)			