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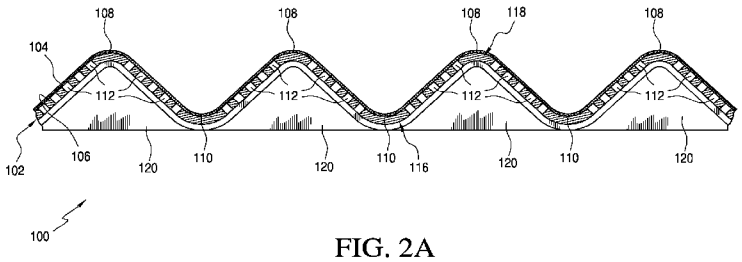

FIG. 2A

(57) Abstract: An improved reactor and process for hydrogen cyanide production, including a catalyst bed comprising a corrugated catalyst support and a knitted catalyst to conform to the wave shape of the corrugated catalyst support.

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PROCESSES FOR PRODUCING HYDROGEN CYANIDE USING CATALYST BED

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. App. No. 61/738,691, filed December 18, 2012, the entire contents and disclosures of which are incorporated herein.

FIELD OF THE INVENTION

[0002] The present invention relates to a process for producing hydrogen cyanide and to a reactor vessel comprising a catalyst bed having a knitted catalyst material and a catalyst support that has a corrugated surface to reduce the cracking and deformation of the knitted catalyst material.

BACKGROUND OF THE INVENTION

[0003] Conventionally, hydrogen cyanide ("HCN") is produced on an industrial scale according to either the Andrussow process or the BMA process. (See e.g., Ullman's Encyclopedia of Industrial Chemistry, Volume A8, Weinheim 1987, pages 161-163). For example, in the Andrussow process, HCN can be commercially produced by reacting ammonia with a methane-containing gas and an oxygen-containing gas at elevated temperatures in a reactor in the presence of a suitable catalyst (U.S. Patent Nos. 1,934,838 and 6,596,251). Sulfur compounds and higher homologues of methane may have an effect on the parameters of oxidative ammonolysis of methane. See, e.g., Trusov, Effect of Sulfur Compounds and Higher Homologues of Methane on Hydrogen Cyanide Production by the Andrussow Method, Russian J. Applied Chemistry, 74:10 (2001), pp. 1693-1697). Unreacted ammonia is separated from HCN by contacting the reactor effluent gas stream with an aqueous solution of ammonium phosphate in an ammonia absorber. The separated ammonia is purified and concentrated for recycle to HCN conversion. HCN is recovered from the treated reactor effluent gas stream typically by absorption into water. The recovered HCN may be treated with further refining steps to produce purified HCN. Clean Development Mechanism Project Design Document Form (CDM PDD, Version 3), 2006, schematically explains the Andrussow HCN production process. Purified HCN can be used in hydrocyanation, such as hydrocyanation of an olefin-containing group, or such as hydrocyanation of 1,3-butadiene and pentenenitrile, which can be used in the manufacture of adiponitrile ("ADN"). In the BMA process, HCN is synthesized from methane and ammonia in

the substantial absence of oxygen and in the presence of a platinum catalyst, resulting in the production of HCN, hydrogen, nitrogen, residual ammonia, and residual methane. (See e.g., Ullman's Encyclopedia of Industrial Chemistry, Volume A8, Weinheim 1987, pages 161-163). Commercial operators require process safety management to handle the hazardous properties of hydrogen cyanide. (See Maxwell et al. Assuring process safety in the transfer of hydrogen cyanide manufacturing technology, JHazMat 142 (2007), 677-684). Additionally, emissions of HCN production processes from production facilities may be subject to regulations, which may affect the economics of HCN manufacturing. (See Crump, Economic Impact Analysis For The Proposed Cyanide Manufacturing NESHAP, EPA, May 2000).

[0004] U.S. Pat. No. 3,033,658 describes a catalyst arranged in a reaction chamber that is supported and rested upon a non-metallic, substantially non-heat conductive, but heat resistant carrier and/or confined or bordered by such non-metallic material. The catalyst may be provided in the form of gauze or a net-like structure.

[0005] U.S. Pat. No. 3,423,185 describes a grate for supporting metallic gauze catalysts in a reactor in which ammonia and methane are reacted to produce HCN, the grate comprising a number of horizontally arranged ceramic blocks with holes therethrough for the passage of reactant gases, the upper part of the grate comprising a catalyst contact means for supporting the gauze catalyst and the lower part of the grate comprising a gas distribution means for uniformly distributing reactant gases across the cross-section of the reactor.

[0006] U.S. Pat. No. 5,356,603 describes a method for producing hydrocyanic acid by using an element which comprises a foraminous structure fabricated from a material consisting essentially of a metal selected from the group consisting of platinum, rhodium, palladium and alloys of mixtures thereof characterized by (a) a novel configuration whereby the initial product of the formula: curve the flat ratio (C/F) multiplied by mesh size and wire diameter, for said element is greater than at least about 0.08 and (b) where, for a given methane and ammonia throughput, the conversion efficiency is a function of the curve to flat ratio (C/F), wire diameter and mesh size combination and conversion efficiency is improved by increasing the mesh size for a given wire diameter, increasing the wire diameter for a given mesh size, and increasing the curve to flat ratio (C/F) to a ratio of above 1.0. The element is woven gauze, knitted fabric, fibers and combinations thereof. The element can be in a series of said elements as a plurality of screens.

[0007] U.S. Pat. No. 5,527,756 describes a catalyst assembly which comprises a plurality of foraminous wire mesh sheets disposed in intimate nested relation to each other along their broad surfaces, the wire sheets defining a non-planar cross-section which consists of a plurality of undulating corrugations. The border of the catalyst assembly is flattened to allow for secure installation in an ammonia converter. The invention includes individual sheets that are stacked adjacent each other, as well as pads comprising multiplicities of sheets that are edge bonded to each other to form integral units. The catalyst assemblies provide a combination of increased surface area and reduced pressure drop that is unique and contributes to improve useful life and corresponding reductions in cost and down time. The catalyst assemblies may be easily manufactured and installed and may be prepared in a variety of sizes and shapes to suit the dimensions and requirements of differing reactors.

[0008] U.S. Pat. No. 7,101,525 describes a catalytic device for carrying out a reaction in a gaseous medium at high temperature, e.g., the synthesis of HCN or the oxidation of ammonia, comprising: at least one textured material, effective as catalyst for the reaction, a support comprising at least one ceramic part, the structure of which makes possible the passage of the gases, the part of the support having a corrugated face, so that the increase in surface area produced by the corrugations with respect to a flat surface is at least equal to that calculated for sawtooth corrugations of between approximately 1.1 and approximately 3. The textured material is positioned so that it is held against the corrugated face of the part of the support and follows the form thereof. The "textured material" is any assemblage of strips or wires which are linear and/or in the form of helical components which makes possible the passage of the gases. This assemblage of the gauze may include woven fabric, knitted fabric or felt type and can be obtained by various techniques, such as weaving, knitting, sewing, embroidery, and the like.

[0009] U.S. Pub. No. 2002/0127932 discusses three-dimensional catalyst gauzes for gas reactions knitted in two or more layers from noble metal wires in which weft threads are inserted between the mesh layers. The mesh layers are preferably joined by pile threads. The weft threads are made from the same type wire material as the mesh and pile threads, namely preferably of platinum-rhodium alloy with from about 4 wt. % to about 12 wt.% rhodium and platinum-palladium-rhodium alloys with from about 4 wt.% to about 12 wt.% palladium and rhodium. Typical alloys are PtRh5, PtRh8 and PtRh10.

[0010] However, existing reactor configurations processes for preparing HCN using these configurations suffer from a number of deficiencies, including catalyst cracking and deformation. Thus, what is needed is an improved HCN reactor configuration and HCN production process.

SUMMARY OF THE INVENTION

[0011] In a first embodiment, the present invention is directed to a catalyst bed for producing hydrogen cyanide, comprising a knitted catalyst material; and a catalyst support having a corrugated surface that abuts the knitted catalyst material, wherein the corrugated surface has a wave shape having one or more rounded valleys to conform the shape of the knitted catalyst to the corrugated surface. The catalyst support may have a substantially uniform thickness. The catalyst bed may further comprise one or more peaks corresponding to the one or more rounded valleys. Each of the one or more rounded valleys may be substantially parallel to adjacent valleys. The corrugated surface may have one or more openings. The one or more openings may be on a sloping portion of the corrugated surface. The one or more openings may have a diameter that is from 0.01 to 3 cm. The corrugated surface may lack sharp edges. The catalyst support may comprise at least 90 wt.% alumina. The corrugated surface has a surface area that is from 1.1 to 3 times the surface area of a planar cross-section of a reactor vessel that holds the catalyst bed. The distance between adjacent valleys on the corrugated surface may be from 2 cm to 15 cm. The knitted catalyst material may comprise a platinum catalyst at least 85 wt.% platinum. The knitted catalyst material may be flexible. The catalyst bed may further comprise an upper catalyst support having a corresponding wave shape to interlock with the shape of the catalyst support.

[0012] In a second embodiment, the present invention is directed to a reaction vessel for producing hydrogen cyanide, comprising a flame arrestor; and a catalyst bed comprising a knitted catalyst material; and a catalyst support having a corrugated surface that abuts the knitted catalyst material, wherein the corrugated surface has a wave shape having one or more rounded valleys to conform the shape of the knitted catalyst to the corrugated surface.

[0013] In a third embodiment, the present invention is directed to a process for producing hydrogen cyanide, comprising: (a) contacting a ternary gas mixture with a catalyst bed comprising a knitted catalyst material and a catalyst support to form a crude hydrogen cyanide product; and (b) recovering hydrogen cyanide. The catalyst support has a corrugated surface that abuts the knitted catalyst material, wherein the corrugated surface has a wave shape having one

or more rounded valleys to conform the shape of the knitted catalyst to the corrugated surface. The catalyst support may have a substantially uniform thickness. The catalyst support may comprise at least 90 wt.% alumina and 10 wt.% or less silica, preferably at least 94 wt.% alumina and 6 wt.% or less silica. The ternary gas mixture may comprise an oxygen-containing gas, a methane-containing gas and an ammonia-containing gas. The oxygen-containing gas may be pure oxygen. The ternary gas mixture may comprise at least 25 vol. % oxygen, preferably 25 to 32 vol. % oxygen. The knitted catalyst material may comprise at least 85 wt.% platinum, preferably at least 90 wt.% platinum. The corrugated surface may have a surface area that is from 1.1 to 3 times the surface area of a planar cross-section of a reactor vessel that holds the catalyst bed. The corrugated surface may comprise one or more rounded peaks corresponding to the one or more rounded valleys to conform the shape of the knitted catalyst to the corrugated surface. The corrugated surface may lack sharp edges. A velocity rate through the catalyst bed may be greater than 2 m/s, preferably greater than 5 m/s, and more preferably greater than 7 m/s. Pressure drop across the catalyst bed may be from 120 kPa to 145 kPa. The corrugated surface may have one or more openings. The one or more openings may be on a sloping portion of corrugated surface. The process may further comprise an upper catalyst support that abuts an upper surface of the knitted catalyst material, wherein the upper catalyst support has a corresponding shape to the catalyst support.

[0014] In a fourth embodiment, the present invention is directed to a catalyst bed for producing hydrogen cyanide, comprising: a knitted catalyst material; and a catalyst support having a corrugated surface that abuts the knitted catalyst material, wherein the corrugated surface has a wave shape having one or more rounded peaks to conform the shape of the knitted catalyst to the corrugated surface.

[0015] In a fifth embodiment, the present invention is directed to a catalyst bed for producing hydrogen cyanide, comprising: a knitted catalyst material; and a catalyst support having a corrugated surface that abuts the knitted catalyst material, wherein the corrugated surface has a wave shape having one or more rounded valleys and corresponding peaks to conform the shape of the knitted catalyst to the corrugated surface.

[0016] In a sixth embodiment, the present invention is directed to a catalyst bed for producing hydrogen cyanide, comprising: a knitted catalyst material; and a catalyst support having a

corrugated surface that abuts the knitted catalyst material, wherein the catalyst support has a substantially uniform thickness and the corrugated surface lacks any sharp edges.

[0017] In a seventh embodiment, the present invention is directed to a catalyst bed for producing hydrogen cyanide, comprising: a knitted catalyst material; and a catalyst support comprising a ceramic foam, wherein the catalyst support has an upper portion and a lower portion and the knitted catalyst material is disposed between the upper portion and the lower portion and contacts a non-planar surface of the upper portion and a non-planar surface of the lower portion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is a simplified schematic flow diagram of an HCN synthesis system according to an embodiment of the presently claimed invention.

[0019] FIG. 2A is a cross-sectional view of a catalyst bed having a corrugated support of the presently claimed invention.

[0020] FIG. 2B perspective view of the catalyst bed of FIG. 2A.

[0021] FIG. 3 is a cross-sectional view of a catalyst bed having a corrugated upper support of the presently claimed invention.

[0022] FIG. 4 is a cross-sectional view of a catalyst bed having a ceramic foam catalyst support of the presently claimed invention.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, group of elements, components, and/or groups thereof.

[0024] Language such as “including,” “comprising,” “having,” “containing,” or “involving,” and variations thereof, is intended to be broad and encompass the subject matter listed thereafter, as well as equivalents, and additional subject matter not recited. Further, whenever a composition, a group of elements, process or method steps, or any other expression is preceded by the transitional phrase “comprising,” “including,” or “containing,” it is understood that it is also contemplated herein the same composition, group of elements, process or method steps or any

other expression with transitional phrases "consisting essentially of," "consisting of," or "selected from the group of consisting of," preceding the recitation of the composition, the group of elements, process or method steps or any other expression.

[0025] The corresponding structures, materials, acts, and equivalents of all means or step plus function elements in the claims, if applicable, are intended to include any structure, material, or act for performing the function in combination with other claimed elements as specifically claimed. The description of the present invention has been presented for purposes of illustration and description, but is not intended to be exhaustive or limited to the invention in the form disclosed. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope and spirit of the invention. The embodiment was chosen and described in order to best explain the principles of the invention and the practical application, and to enable others of ordinary skill in the art to understand the invention for various embodiments with various modifications as are suited to the particular use contemplated. Accordingly, while the invention has been described in terms of embodiments, those of skill in the art will recognize that the invention can be practiced with modifications and in the spirit and scope of the appended claims.

[0026] Reference will now be made in detail to certain disclosed subject matter. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that they are not intended to limit the disclosed subject matter to those claims. On the contrary, the disclosed subject matter is intended to cover all alternatives, modifications, and equivalents, which can be included within the scope of the presently disclosed subject matter as defined by the claims.

[0027] Hydrogen cyanide ("HCN") is produced on an industrial scale according to either the Andrussow process or by the BMA process. In the Andrussow process, methane, ammonia and oxygen-containing raw materials (also referred to herein as "reactants") are reacted at temperatures above 1000°C in the presence of a catalyst to produce a crude hydrogen cyanide product comprising HCN, hydrogen, carbon monoxide, carbon dioxide, nitrogen, residual ammonia, residual methane, and water. Natural gas is typically used as the source of methane while air, oxygen-enriched air, or pure oxygen can be used as the source of oxygen. The catalyst is typically a wire mesh platinum/rhodium alloy or a wire mesh platinum/iridium alloy. Other catalyst compositions can be used and include, but are not limited to, a platinum group metal,

platinum group metal alloy, supported platinum group metal or supported platinum group metal alloy. Other catalyst configurations can also be used and include, but are not limited to, porous structures, wire gauze, tablets, pellets, monoliths, foam, impregnated coatings, and wash coatings. However, at reaction startup and shutdown, as well as during the reaction, the catalyst may crack or deform. Catalyst cracking may allow reactant bypass, thus reducing conversion of reactants to HCN, reducing HCN yield, and allowing unwanted reactions downstream. Catalyst deformation may require the flow rate of the reactants to be reduced, thus reducing HCN yield. These difficulties may be partially alleviated by using a catalyst bed, comprising the catalyst on a support. However, the catalyst may still be subject to cracking and deformation. Additionally, depending on the support used, the catalyst bed may require reducing the reactant flow.

[0028] Surprisingly and unexpectedly, catalyst cracking and deformation have been reduced and/or eliminated by using a knitted platinum catalyst on a corrugated support. The knitted platinum catalyst may comprise greater than 85 wt.% platinum, e.g., 90 wt.% platinum. Catalyst is loaded in a reaction vessel to a catalyst loading in the range from 0.7 to 1.4 (g catalyst)/(kg feed gas/hr). The knitted catalyst may further comprise one or more metals selected from the group consisting of nickel, cobalt, palladium, rhodium, ruthenium, iridium, gold, silver and copper. In some embodiments, the knitted catalyst comprises 90 wt.% platinum and 10 wt.% rhodium (90/10). When placed on a planar catalyst support, a knitted catalyst comprising 90 wt.% platinum and 10 wt.% rhodium may not be able to withstand higher production rates and may be subject to deformation, cracking, and/or shrinkage. Thus, a flat support may require a 85/15 platinum/rhodium catalyst to have sufficient strength to withstand higher production rates. The higher production rates may be due to operating with oxygen-enriched air or pure oxygen and from operating at a high velocity rate through the catalyst bed. The velocity should be sufficient to overcome the flashback velocity. In one aspect, the velocity rate through the catalyst bed is at least 2 m/s, e.g., at least 5 m/s or at least 7 m/s. As the velocity increases, there may be a larger pressure difference on the catalyst bed that causes the bed to compress. For example, the pressure difference on the catalyst bed may be from 120 to 145 kPa, e.g., from 125 to 140 kPa. If the catalyst bed lacks sufficient strength, then the catalyst bed may crack under high velocity rates. To improve the strength of a knitted catalyst comprising 90 wt.% platinum and 10 wt.% rhodium, a catalyst bed having a corrugated support is advantageously used. This allows for higher production rates without causing damage to the knitted catalyst. Typically, a

catalyst with 90 wt.% platinum has a shorter lifetime compared with a catalyst with 85 wt.% platinum. Advantageously, the lifetime of the 90 wt.% platinum catalyst may be extended up to two or more preferably three times the lifetime of a catalyst comprising 85 wt.% platinum using a corrugated support of the present invention. In addition, the lifetime of a 85 wt.% platinum catalyst may also be increased using the corrugated support of the present invention

[0029] The reactant gases to produce HCN include an ammonia-containing gas, a methane-containing gas and an oxygen-containing gas. The reactant gases are mixed prior to entering the reactor, to form a ternary gas mixture. In some embodiments, the ternary gas mixture comprises at least 25 vol.% oxygen, e.g., from 25 to 32 vol.% oxygen, or from 26 to 30 vol.% oxygen. The oxygen-containing gas may be air, oxygen-enriched air or pure oxygen. Using oxygen-enriched air or pure oxygen offers the opportunity to reduce the size and operating cost of downstream equipment that would otherwise be necessary to process a large volume of inert nitrogen present in air. In one embodiment, oxygen-containing gas comprises greater than 21 vol.% oxygen, e.g. greater than 28 vol.% oxygen, greater than 80 vol.%, greater than 90 vol.%, greater than 95 vol.% or greater than 99 vol.% oxygen. The ternary gas mixture may have a molar ratio of ammonia-to-oxygen from 1.2 to 1.6, e.g., from 1.3 to 1.5, a molar ratio of ammonia-to-methane from 1 to 1.5, e.g., from 1.1 to 1.45 and a molar ratio of methane-to-oxygen from 1 to 1.25, e.g., from 1.05 to 1.15. For example, a ternary gas mixture may have a molar ratio of ammonia-to-oxygen of 1.3 and methane-to-oxygen 1.2. In another exemplary embodiment, the ternary gas mixture may have a molar ratio of ammonia-to-oxygen of 1.5 and methane-to-oxygen of 1.15. The oxygen concentration in the ternary gas mixture may vary depending on these molar ratios.

[0030] As described herein, using a combination of a knitted platinum catalyst and a corrugated support may reduce catalyst cracking and deformation. Catalyst cracking may allow reactant bypass, e.g., reactants passing through the catalyst bed without reacting. Oxygen, methane and ammonia content in the crude hydrogen cyanide product are carefully controlled and bypass of the catalyst bed has consequences for each reactant. Further, because the content of oxygen, methane and ammonia are carefully controlled, bypass of the reactants makes controlling the amount of reactant in the crude hydrogen cyanide product difficult. When methane bypasses the catalyst bed, nitrile byproducts may accumulate in the HCN separation train. When oxygen bypasses the catalyst bed, a system upset, including a possible detonation event, may occur. When ammonia bypasses the catalyst bed, downstream ammonia recovery will have to be

adjusted to handle the varied amounts of ammonia. Catalyst deformation may require reduction of the flow rate of the ternary gas mixture, causing a concomitant reduction in HCN production rate. This may exacerbate possible inefficiencies in producing the desired crude hydrogen cyanide product and leading to loss production.

[0031] In general, FIG. 1 shows a HCN synthesis system 10. Generally, the HCN is produced in a reaction assembly 12 comprising an elongated conduit 14 and a reactor vessel 16. In the Andrussow process, the reactant gases, which include an oxygen-containing gas 18, a methane-containing gas 20, and an ammonia-containing gas 22, are introduced into the elongated conduit 14. It is noted that the feed locations shown in FIG. 1 are schematic and are not intended to show an order for feeding the reactants to the elongated conduit 14. In some embodiments, methane-containing gas 20 and ammonia-containing gas 22 may be combined prior to being introduced to elongated conduit 14. In one embodiment, elongated conduit 14 may contain one or more static mixing zones having tabs for producing a thoroughly mixed ternary gas 24. In one embodiment, the ternary gas mixture 24 comprises at least 25 vol.% oxygen. Ternary gas mixture 24 exits elongated conduit 14 and contacts a catalyst contained within reactor vessel 16 to form a crude hydrogen cyanide product 26 containing HCN. Catalyst may be within a catalyst bed 100 having a corrugated catalyst support, as described further herein.

[0032] Prior to contacting the catalyst bed 100, ternary gas mixture contacts a distributor plate 28 that has a plurality of holes to assist in distributing the ternary gas mixture and breaking any jet flow within reactor vessel 16. In one embodiment, distributor plate 28 has a void area from 50 to 80% of the total surface thereof. The HCN synthesis reaction that occurs in the reaction vessel is an exothermic reaction conducted at a reaction temperature in the range of 1000°C to 1250°C and a pressure in the range of 100 kPa to 400 kPa. Reactor vessel 16 may also comprise a flame arrestor 30, a radiation shield 32 adjacent to catalyst bed 100 and an undersupport 34. An igniter hole 36 may extend through radiation shield 32 to enable an igniter to touch the upper surface of catalyst bed 100. Other ignition techniques that do not require a hole in radiation shield 32 may be used with embodiments of the present invention. The ignition of catalyst bed 100 can be carried out in any manner known to those skilled in the art.

[0033] Reactor vessel 16 may also comprise a heat exchanger 38, e.g., waste heat boiler, for cooling crude hydrogen cyanide product 26. Ammonia can be recovered from crude hydrogen cyanide product 26 in an ammonia recovery section 40 and returned via line 42. The

HCN can be further refined in an HCN refining section 44 to a purity required for the desired use. In some embodiments, the HCN may be a high purity HCN containing less than 100 mpm water.

[0034] FIG. 2A and 2B show a catalyst bed 100 of the present invention. In the cross-sectional view in FIG. 2A, catalyst bed 100 comprises catalyst support 102 that provides strength and rigidity to maintain a corrugated shape for knitted catalyst material 104. Catalyst support 102 and knitted catalyst material 104 are permeable to allow the passage of gases. Knitted catalyst material 104 may comprise a plurality of layers that are stacked. Knitted catalyst material 104 may have a mesh size from 15 to 40 openings per linear cm and with wire diameter from 0.076 mm to about 0.228 mm. For purposes of the present invention, a woven material is not used in catalyst bed 100.

[0035] Catalyst support 102 has a corrugated surface 106, that is wave shaped, upon which the knitted catalyst material 104 abuts. As shown, corrugated surface 106 abuts a lower surface of the knitted catalyst material 104. Catalyst support 102 maintains a uniform flow over corrugated surface 106. In one embodiment, the knitted catalyst material 104 is flexible and is able to form to the shape of the corrugated surface 106. In other embodiments, the knitted catalyst material 104 may have a rigid shape that is formed to correspond to the wave shape of the corrugated surface 106. Knitted catalyst material 104 is preferably not adhered or fastened to the corrugated surface 106.

[0036] Catalyst support 102 comprises a plurality of peaks 108 and valleys 110. The number of peaks 108 and valleys 110 may vary depending on the diameter of the reactor vessel. Preferably, the number of peaks 108 corresponds to the number of valleys 110, and may vary, e.g., ranging from 2 to 500. In one embodiment, the surface area of corrugated surface 106 may be from 1.1 to 3, e.g., 1.1 to 1.5 times the surface area of a planar cross-section of the reactor vessel. This increased surface area allows for an increase in the loading of catalyst which can lead to further increases in productivity. In one embodiment, valleys 110 are curved or rounded to eliminate any sharp edges. Corresponding peaks 108 may also be curved or rounded. Without being bound by theory, the knitted catalyst material 104 may tend to crack in the sharp edge that are formed from a sawtooth, square, or triangle shaped corrugated support. Damage may be acute in the sharp edges that results in increased bypass of reactants into the crude hydrogen cyanide product. Advantageously, rounded peaks 108 and valleys 110 eliminate the sharp edges on the

corrugated surface 106. The lack of sharp edges, especially having an angle of 90°, may further reduce the cracking of the knitted catalyst material 104 and improve the strength of the knitted catalyst material 104 to operate at higher production rates. In addition, the bypass of reactants may be reduced significantly.

[0037] In one embodiment, the height from valley to peak is from 0.05 cm to 10 cm, e.g., 0.1 cm to 3.5 cm. Optionally, the height of catalyst support 102 may be substantially uniform. The distance from valley to adjacent valley depends on the size of the corrugated surface and may be from 2 cm to 15 cm, e.g., 4 to 15 cm, or 4 cm to 10 cm. The distance between adjacent valleys may be equal to the distance between adjacent peaks. Each peak and valley is substantially parallel to the adjacent peak and valley across the width of catalyst support 102.

[0038] On the corrugated surface 106, there may be a plurality of openings 112. The number of openings 112 may vary from 0.5 openings per square cm to 5 openings per square cm, e.g, from 1 opening per square cm to 2 openings per square cm. Openings 112 create perforations that extend through the thickness of the catalyst support and allow gases to pass there-through. Openings 112 may be circular, oval, square, rectangular, triangular, or other polygonal shape. The maximum diameter of openings may be from 0.01 cm to 3 cm, e.g., from 0.05 to 1.5 cm. There may also be one or more indents (not shown) that are depressions on the corrugated surface that not do extend through the thickness. Indents do not directly contact the knitted catalyst material 102. In one embodiment, indents may separate openings 112.

[0039] Openings 112 may be arranged in any pattern on the corrugated surface 106. In one embodiment, the valley region 116 that is closest to the valley 110 may be solid and does not contain any openings 112. Valley region 116 may receive the greatest stress under high production rates and preventing gas from passing through valley region 116 may reduce the stress on valley region 116. Likewise, the peak region 118 that is closest to the peak 108 may also be solid. Thus, the one or more openings are on a sloping portion of the corrugated surface. This may prevent gases from collecting in either the valley 110 or peak 108 and reduces the possibility of cracking of knitted catalyst material 104 that is adjacent to the valley region 116 or peak region 108. In other embodiments, the peaks and/or valleys may contain openings 112 thereto. In particular, there may openings in valley region 116 or peak region 108 to allow gases to pass therethrough.

[0040] In one embodiment, the thickness of catalyst support 102 may be substantially uniform and range from 0.2 cm to 2 cm, e.g., from 0.25 cm to 0.75 cm. If the catalyst support is too thin, it may lack structural integrity. Conversely, if the support is too thick, it may be susceptible to cracking due to increases in pressure. The thickness of knitted catalyst material 104 may also be substantially uniform. A substantially uniform thickness refers to a thickness that does not vary by more than 5%, e.g., more than 1%. This provides a lower surface 118 that has a similar wave shape as corrugated surface 106. A substantially uniform thickness allows a uniform pressure drop across catalyst support 102. In other catalyst supports, there may be thicker area under the peak which causes the gases to follow towards the thinner valley area and increases the pressure in the valley. An increase in pressure may lead to cracking of the knitted catalyst material.

[0041] The pressure drop across catalyst bed 100 may be withstood by using the corrugated shape of the catalyst support with a substantially uniform thickness. The pressure drop of a corrugated substantially uniform thickness support is less than comparative supports that have varied support thickness. Under high production rates, eg., high velocity, the pressure drop across the catalyst bed 100 may be from 120 to 145 kPa, e.g., from 125 to 140 kPa.

[0042] Also on lower surface there may one or more ribs 120 for providing support to the catalyst support 102. Ribs 120 may be evenly spaced across the width of the catalyst support 102. In addition, ribs may be placed on the exterior edge of the catalyst support 102. Ribs may define cavities on the lower surface. Ribs may rest upon a shelf along the edge of the internal catalyst wall and/or on an undersupport. Catalyst support 102 may be rectangular, oval or circle in shape to fit into the reaction vessel 16. In some embodiments, catalyst support 102 may be divided into portions that can be arranged in the reaction vessel 16.

[0043] Catalyst support 102 may have a unibody assembly that is made of a ceramic composite that comprises at least 90 wt.% alumina, e.g., at least 94 wt.% alumina. The ceramic composite is capable of withstanding the high operating temperatures of the reaction. Preferably, the ceramic composite contains low amounts of silicon, such as silica and other oxides or compounds of silicon. In one embodiment, the ceramic composite may contain less than 10 wt.% silica, e.g., less than 6 wt.% and more preferably less than 1 wt.%. Other oxides, including but not limited to oxides of titanium, zirconium, cerium, yttrium, calcium, and combinations thereof, may be used in the ceramic composite. In addition, the ceramic composite may be

substantially free of magnesium. In one embodiment, to control the openings and reduce stress in the valley region, it is preferred that catalyst support 102 is not a ceramic foam.

[0044] In one embodiment, when operating with oxygen-containing gas comprising oxygen-enriched air or pure oxygen stream, i.e. a ternary gas mixture containing at least 25 vol.% oxygen, additional hydrogen may be formed in the crude product. In one embodiment, the crude product may comprise from 20 to 50 vol.% hydrogen, e.g., from 30 to 40 vol.% hydrogen or from 34 to 36 vol.% hydrogen. Hydrogen may increase the vaporization and redeposition of silica that may be leached from silicate-containing refractories in a reducing and high temperature environment. Thus, if silica is present in the catalyst support, then the presence of hydrogen may cause deformation or cracking of the catalyst support. In one embodiment, the ceramic composite may be substantially free of silicon, including oxides, such as silica, and compounds thereof.

[0045] In some embodiments, in addition to catalyst support 102 there may be a radiation shield 130 that is placed upstream of knitted catalyst material 104 as shown in FIG. 3. Upper catalyst support 120 may have the corresponding structure of catalyst support 102 but is inverted to interlock catalyst material 104 between catalyst support 102 and upper catalyst support 120. In addition, radiation shield 130 may also have corresponding upper ribs 132. This may control the expansion of gases during the reaction from impacting the knitted catalyst material 104. In addition, the upper catalyst support may be in direct contact with one or more insulating and refractory layers.

[0046] In FIG. 4, there is provided a catalyst bed 200 having a ceramic foam catalyst support 202 and knitted catalyst material 204 as described herein. Ceramic foam may have a non-uniform cross-section that allows for the passage of gas through pores. Ceramic foam may be made from at least 90 wt.% alumina, e.g., at least 94 wt.% alumina. The ceramic foam contains low amounts of silicon or oxides and compounds thereof, e.g., 10 wt.% or less, 6 wt.% or less, or 1 wt.% or less.

[0047] There may be an upper portion 206, e.g., radiation shield, and lower portion 208 that surround knitted catalyst material 204. Upper portion 206 has a non-planar surface 210 that contacts knitted catalyst material 204 and an opposing planar surface 212. Lower portion 208 also has a non-planar surface 214 that contacts knitted catalyst material 204 and an opposing planar surface 216. Each non-planar surface, e.g., corrugated surface, may be a wave-like shape

that has a pattern of peaks and valleys. Thus, the thickness of upper portion 206 and lower portion 208 may vary depending on the non-planar surface. In one embodiment, the peaks and valleys formed by the wave-like shape may have a uniform or irregular pattern. In one embodiment, upper portion 206 may be an equidistance from lower portion 208.

[0048] Returning to elongated conduit 14, there may be one or more mixers (not shown) for mixing the reactant gases to form ternary gas mixture 24. The mixers are shaped and sized so as to be able to thoroughly and quickly mix the reactant gases, i.e., to form a thoroughly mixed ternary gas mixture. The mixers may be any mixers that function in the manner described herein. Nonlimiting examples of mixers which may be employed in the practice of the present invention are binary mixers, ternary mixers, bustle mixers, static mixers, and the like. The dimensions of the mixers can vary widely and will be dependent, to a large degree, on the capacity of the reactor vessel.

[0049] A thoroughly mixed ternary gas for the purposes of the present invention has a CoV that is less than 0.1 across the diameter of the catalyst bed, or more preferably less than 0.05 and even more preferably of less than 0.01. In terms of ranges, the CoV may be from 0.001 to 0.1, or more preferably from 0.001 to 0.05. Low CoV beneficially increases the productivity of reactants being converted to HCN. A thoroughly mixed ternary gas advantageously increases the productivity of HCN and returns higher yields of HCN. When CoV exceeds 0.1, the reactant gases may be in concentrations that are outside the safe operating ranges for the catalyst bed. For example, when operating at higher oxygen concentrations in the ternary gas, a larger CoV may create an increase in oxygen that results in a flashback. In addition, when CoV is larger the catalyst bed may be exposed to more methane, which may lead to a buildup of carbon deposits. The carbon deposits may decrease catalyst life and performance. Thus, there may be a higher raw material requirement with larger CoV.

[0050] In one embodiment, the mixer may also comprise an optional flow straightener (not shown). Optional flow straighteners may have a configuration to align the flow prior to the gases contacting a static mixing zone. Flow straighteners may also distribute the gas around the entire area of the conduit and substantially prevent the reactant gases from passing directly down the middle of conduit. Flow straighteners, when used, may be positioned downstream of each inlet port and upstream to the static mixer(s).

[0051] A flame arrestor may be spatially disposed above the catalyst bed so as to provide

a space there between. The flame arrestor quenches any upstream burning resulting from flash back within the reaction vessel. Ceramic foam may be disposed along at least a portion of an interior wall of the housing defining the internal reaction chamber and the catalyst. The ceramic foam minimizes feed gas bypass due to catalyst shrinkage when the reactor is shut down. Ceramic foam disposed above the catalyst bed functions to minimize ternary gas volume and reduce pressure drop. Ferrules are disposed in each of the outlets of the housing and provide fluid communication between the catalyst bed and an upper portion of a waste heat boiler. An undersupport having a substantially honeycomb configuration to reduce pressure drop across the undersupport. Undersupport may be disposed substantially adjacent a lower surface of the catalyst bed, e.g., lower surface of the corrugated catalyst support.

[0052] Various control systems may be used to regulate the reactant gas flow. For example flow meters that measure the flow rate, temperature, and pressure of the reactant gas and allow a control system to provide "real time" feedback of pressure- and temperature-compensated flow rates to operators and/or control devices may be used. As will be appreciated by one skilled in the art, the foregoing functions and/or process may be embodied as a system, method or computer program product. For example, the functions and/or process may be implemented as computer-executable program instructions recorded in a computer-readable storage device that, when retrieved and executed by a computer processor, controls the computing system to perform the functions and/or process of embodiments described herein. In one embodiment, the computer system can include one or more central processing units, computer memories (e.g., read-only memory, random access memory), and data storage devices (e.g., a hard disk drive) The computer-executable instructions can be encoded using any suitable computer programming language (e.g., C++, JAVA, etc.). Accordingly, aspects of the present invention may take the form of an entirely software embodiment (including firmware, resident software, micro-code, etc.) or an embodiment combining software and hardware aspects.

[0053] From the above description, it is clear that the present invention is well adapted to carry out the objects and to attain the advantages mentioned herein as well as those inherent in the presently provided disclosure. While preferred embodiments of the present invention have been described for purposes of this disclosure, it will be understood that changes may be made which will readily suggest themselves to those skilled in the art and which are accomplished within the spirit of the present invention.

[0054] The invention can be further understood by reference to the following examples.

Example 1

[0055] A ternary gas mixture is formed by combining pure oxygen, an ammonia-containing gas and a methane-containing gas. The reactant gases are fed at a methane-to-oxygen molar ratio of 1.2 and an ammonia-to-oxygen molar ratio of 1:1.5 to produce a ternary gas mixture containing approximately 28.5 vol.% oxygen. The ternary gas mixture is fed at high velocity rates of greater than 7.3 m/s. The ternary gas mixture reacts at a temperature from 1000 to 1200°C in the presence of a platinum/rhodium catalyst to form a crude hydrogen cyanide product. The platinum/rhodium catalyst comprises 90 wt.% platinum and 10 wt.% rhodium (90/10). The platinum/rhodium catalyst is knitted and is supported by a corrugated support having 12 rounded valleys and peaks. The corrugated support does not have sharp edges. The distance between each peak is from 10 to 10.5 cm. The corrugated support has a height from the base to the peak of 5 cm and a height to the valley of 2 cm, and uniform thickness. The corrugated support is ceramic and comprises more than 90 wt.% alumina and less than 10 wt.% silica. The corrugated surface has a surface area that is 1.4 times the surface area of a planar cross-section of a reactor vessel. The corrugated support has about 1.7 openings per square cm (11 openings per square inch), except in the valleys which are solid. The corrugated support abuts the knitted catalyst and has a wave shape that conforms to the shape of the knitted catalyst to the corrugated support. The rounded valleys and wave shape of the corrugated support minimize catalyst deformation and the flow rate of the ternary gas mixture is not adjusted. Further no cracking is observed in the catalyst after 150 to 180 days of continuous operation. The HCN yield is improved 0.5 to 2%. The catalyst lifetime increases relative to the Comparative Examples.

Example 2

[0056] The process and apparatus are the same as in Example 1, except that the catalyst comprises 85 wt.% platinum and 15 wt.% rhodium (85/15). No cracking is observed in the catalyst after 150 to 180 days of continuous operation. Although the knitted catalyst does not deform and catalyst lifetime increases, at the same flow rates of Example 1 the HCN yield is less than Example 1. This is due to the lower loadings of platinum in the knitted catalyst.

Comparative Example A

[0057] The process and apparatus are the same as in Example 1, except that the corrugated support comprises 15 wt.% silica. After reaction start-up, the silica in the corrugated support degrades due to the increased hydrogen concentration in the crude hydrogen cyanide product and the corrugated support collapses.

Comparative Example B

[0058] The process and apparatus are the same as in Example 1, except that the support is flat and is not corrugated. Using a 90/10 platinum/rhodium catalyst, the catalyst deforms shortly after reaction start-up. Further cracking is observed in the catalyst.

Comparative Example C

[0059] The 90/10 platinum/rhodium catalyst gauze is supported by a corrugated support having a sawtooth configuration having sharp edges as shown in US Pat. No. 7,101,525. Feeding the reactant gases at high velocity rates (of greater than 7.3 m/s) compresses the catalyst gauze and the catalyst gauze would crack in the sharp edges, leading to yield decrease. This leads to a reactor shut down.

Comparative Example D

[0060] The process and apparatus are the same as in Example 1, except that the 90/10 platinum/rhodium catalyst is woven and is supported by a ceramic foam support having a wave shape similar to Example 1. After reaction start-up, the catalyst exhibits cracking, especially in the valleys. This leads to increase leakage of reactants through the catalyst bed.

We claim:

1. A process for producing hydrogen cyanide, comprising:

(a) contacting a ternary gas mixture with a catalyst bed comprising a knitted catalyst material and a catalyst support to form a crude hydrogen cyanide product; and

(b) recovering hydrogen cyanide;

wherein the catalyst support has a corrugated surface that abuts the knitted catalyst material, wherein the corrugated surface has a wave shape having one or more rounded valleys to conform the shape of the knitted catalyst to the corrugated surface.

2. The process of claim 1, wherein the catalyst support has a substantially uniform thickness.

3. The process of any of the preceding claims, wherein the catalyst support comprises at least 90 wt.% alumina and 10 wt.% or less silica, preferably at least 94 wt.% alumina and 6 wt.% or less silica.

4. The process of any of the preceding claims, wherein the ternary gas mixture comprises an oxygen-containing gas, a methane-containing gas and an ammonia-containing gas.

5. The process of claim 4, wherein the oxygen-containing gas is pure oxygen.

6. The process of any of the preceding claims, wherein the ternary gas mixture comprises at least 25 vol. % oxygen, preferably 25 to 32 vol. % oxygen.

7. The process of any of the preceding claims, wherein the knitted catalyst material comprises at least 85 wt.% platinum, preferably at least 90 wt.% platinum.

8. The process of any of the preceding claims, wherein the corrugated surface has a surface area that is from 1.1 to 3 times the surface area of a planar cross-section of a reactor vessel that holds the catalyst bed.

9. The process of any of the preceding claims, wherein the corrugated surface further comprises one or more rounded peaks corresponding to the one or more rounded valleys to conform the shape of the knitted catalyst to the corrugated surface.

10. The process of any of the preceding claims, wherein the corrugated surface lacks sharp edges.

11. The process of any of the preceding claims, wherein a velocity rate through the catalyst bed is greater than 2 m/s, preferably greater than 5 m/s, and more preferably greater than 7 m/s.

12. The process of any of the preceding claims, wherein pressure drop across the catalyst bed is from 120 kPa to 145 kPa.

13. The process of any of the preceding claims, wherein the corrugated surface has one or more openings.

14. The process of claim 13, wherein the one or more openings are on a sloping portion the of corrugated surface.

15. The process of any of the preceding claims, further comprising an upper catalyst support that abuts an upper surface of the knitted catalyst material, wherein the upper catalyst support has a corresponding shape to the catalyst support.

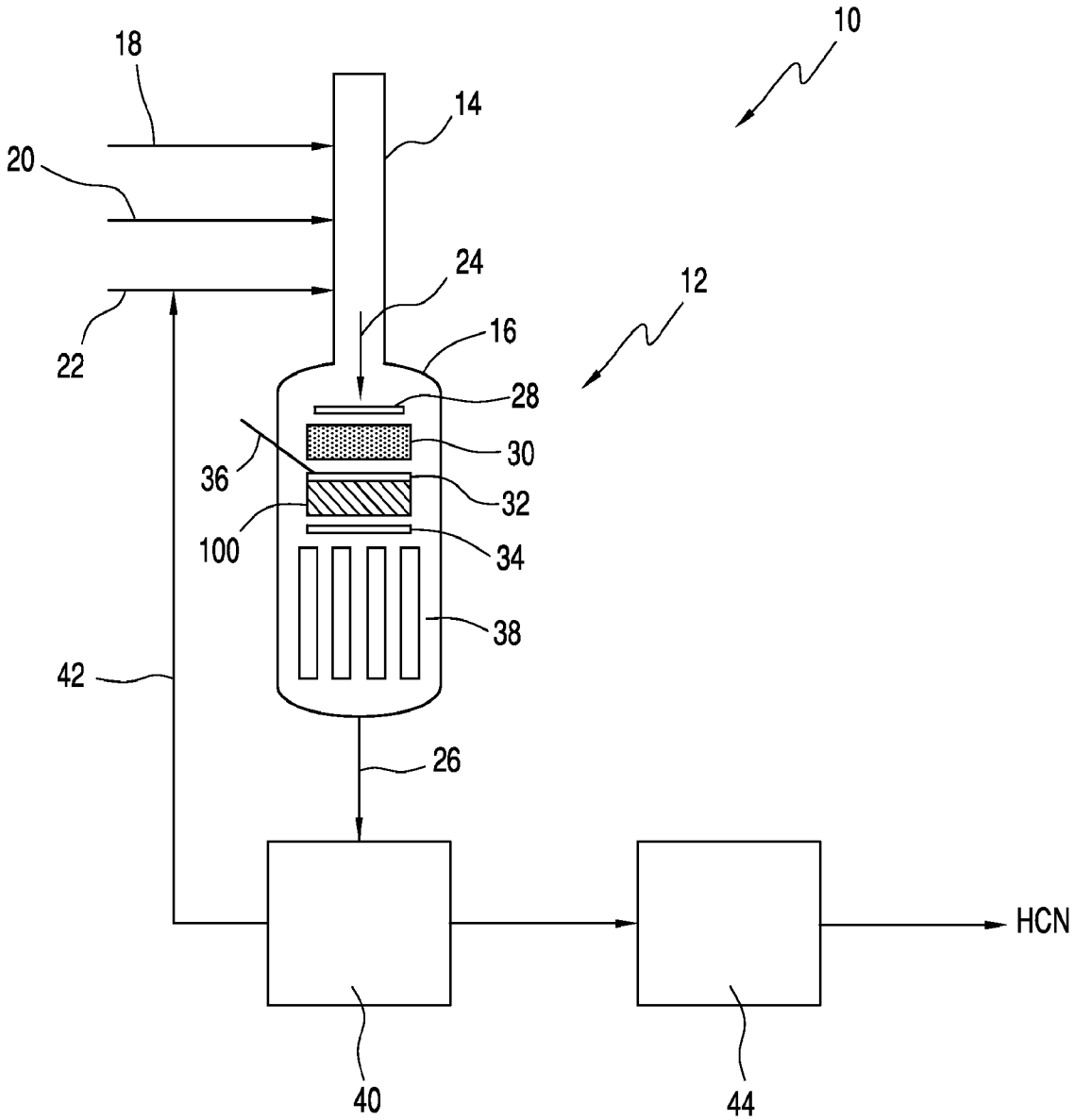

FIG. 1

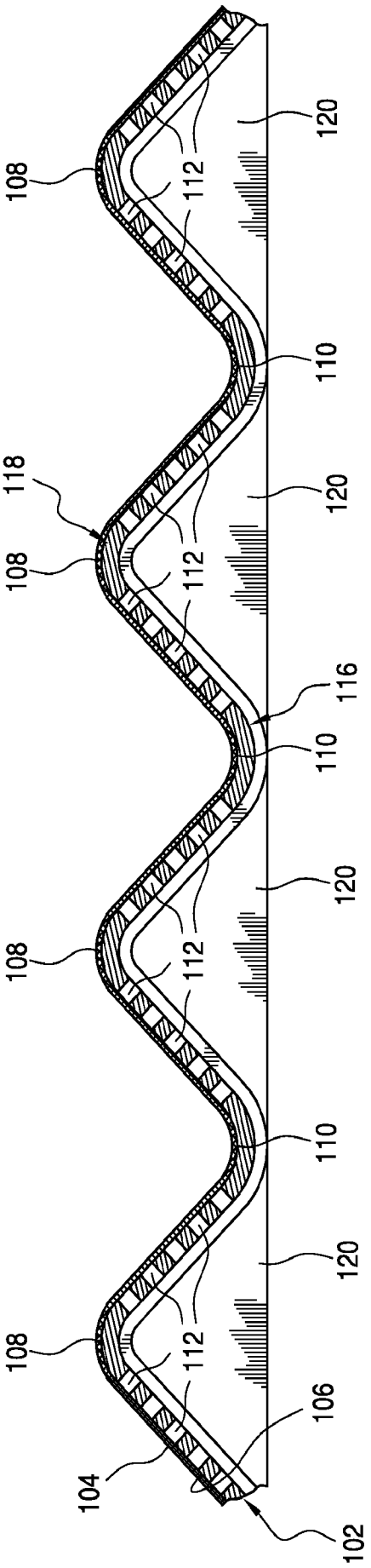
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FIG. 2A

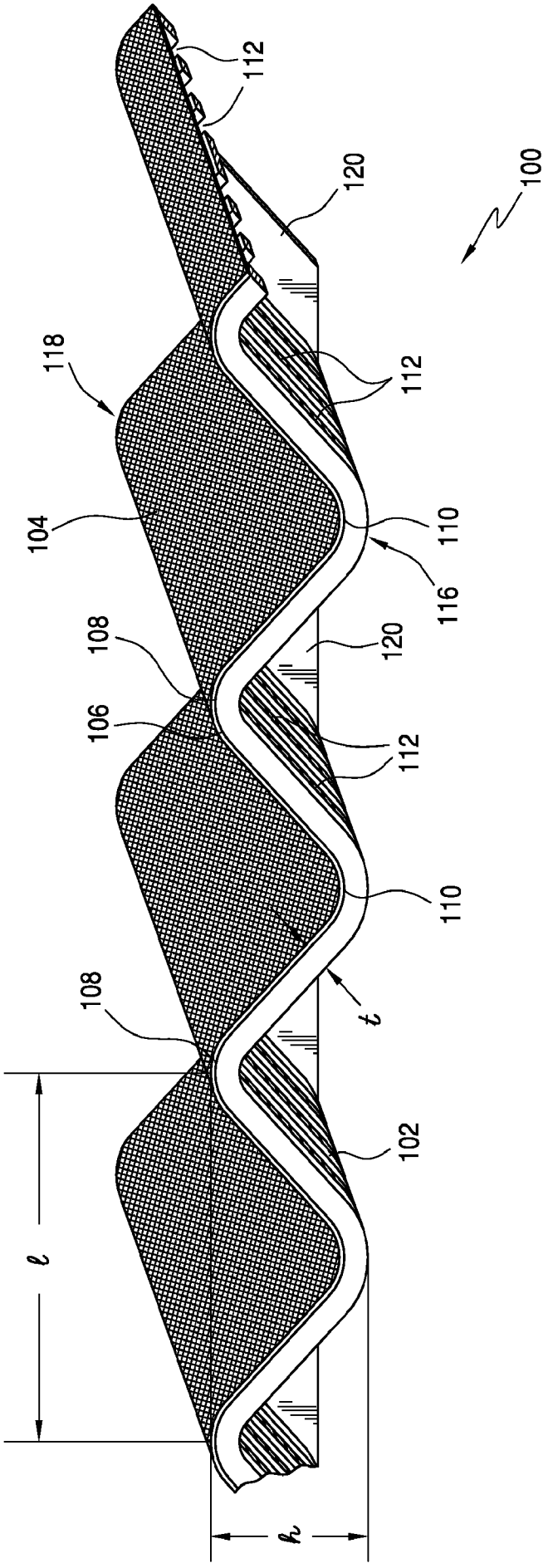

FIG. 2B

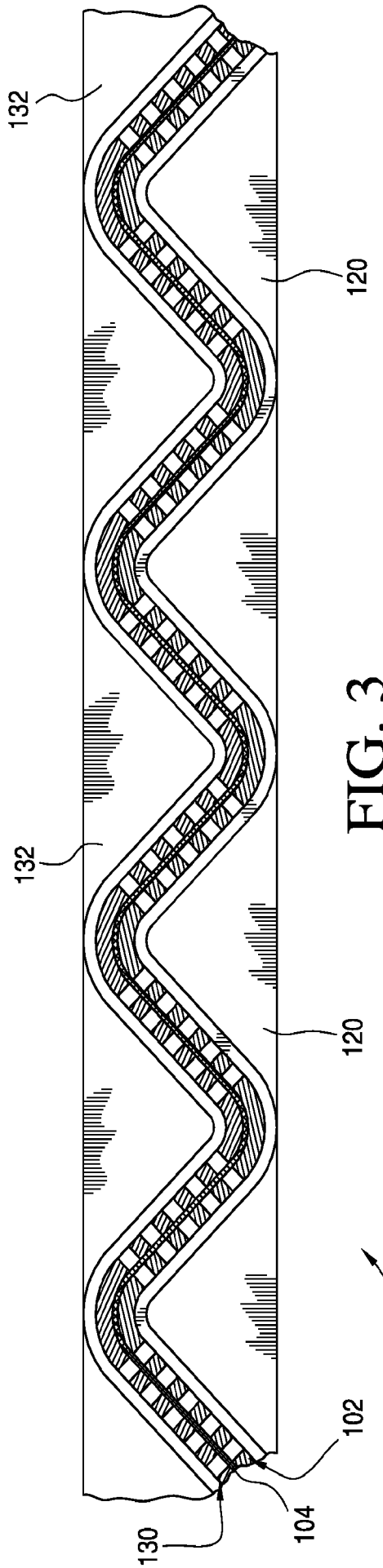
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FIG. 3

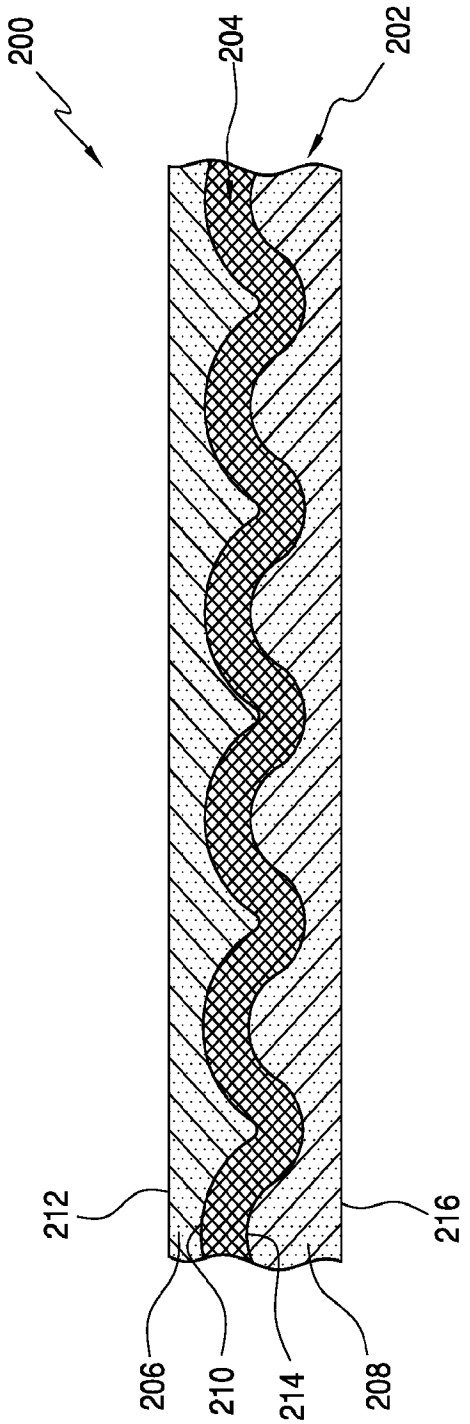
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FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/074612

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01C3/02 B01J23/44 B01J32/00 B01J33/00 B01J35/04 B01J35/06
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01C B01J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/175195 A1 (STEFFEN JOSEPH [FR]) 18 September 2003 (2003-09-18) cited in the application paragraphs [0011] - [0015], [0020], [0029], [0034]; figure 1	1-15
A	CA 809 578 A (UNION CARBIDE CORP) 1 April 1969 (1969-04-01) page 6, line 11 - page 8, line 25; claims 1,3	1-15
A	EP 0 519 699 A1 (JOHNSON MATTHEY PLC [GB]) 23 December 1992 (1992-12-23) page 3, line 41 - page 4, line 44	1-15
A	JP H08 224482 A (MATSUSHITA ELECTRIC IND CO LTD) 3 September 1996 (1996-09-03) paragraphs [0016], [0017], [0022] - [0024]; claims 1,2; figure 1	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 April 2014	12/05/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Werner, Håkan

INTERNATIONAL SEARCH REPORT

Information on patent family members

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