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Gerhold

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[45] **Sept. 2, 1975**

[54] **CERAMIC HONEYCOMB STRUCTURE FOR ACCOMMODATING COMPRESSION AND TENSION FORCES**

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[52] **U.S. Cl.** .... **428/116;** 23/288 FC; 156/89; 428/118

[51] **Int. Cl.**^{2} **B32B 3/12**

[58] **Field of Search** .... 29/455 LM; 161/68, 69; 156/89, 197; 23/288 F, 288 FC; 52/615, 618; 181/36 C, 71; 252/477 R

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[57] **ABSTRACT**

An improved ceramic honeycomb structure is provided by having a configuration with thin curved walls between the multiplicity of cells whereby both compression and tension forces can be better accommodated when the structure is being subjected to non-uniform temperature conditions. Two or more sets of opposing curved walls can be used to define each cell of the multiplicity thereof and the curvature for each set of walls is such as to permit elongative deformation in one direction without causing a reduced width cell or a closer spacing for juncture lines between adjacent cells in a direction transverse to the expansion movement.

4 Claims, 6 Drawing Figures

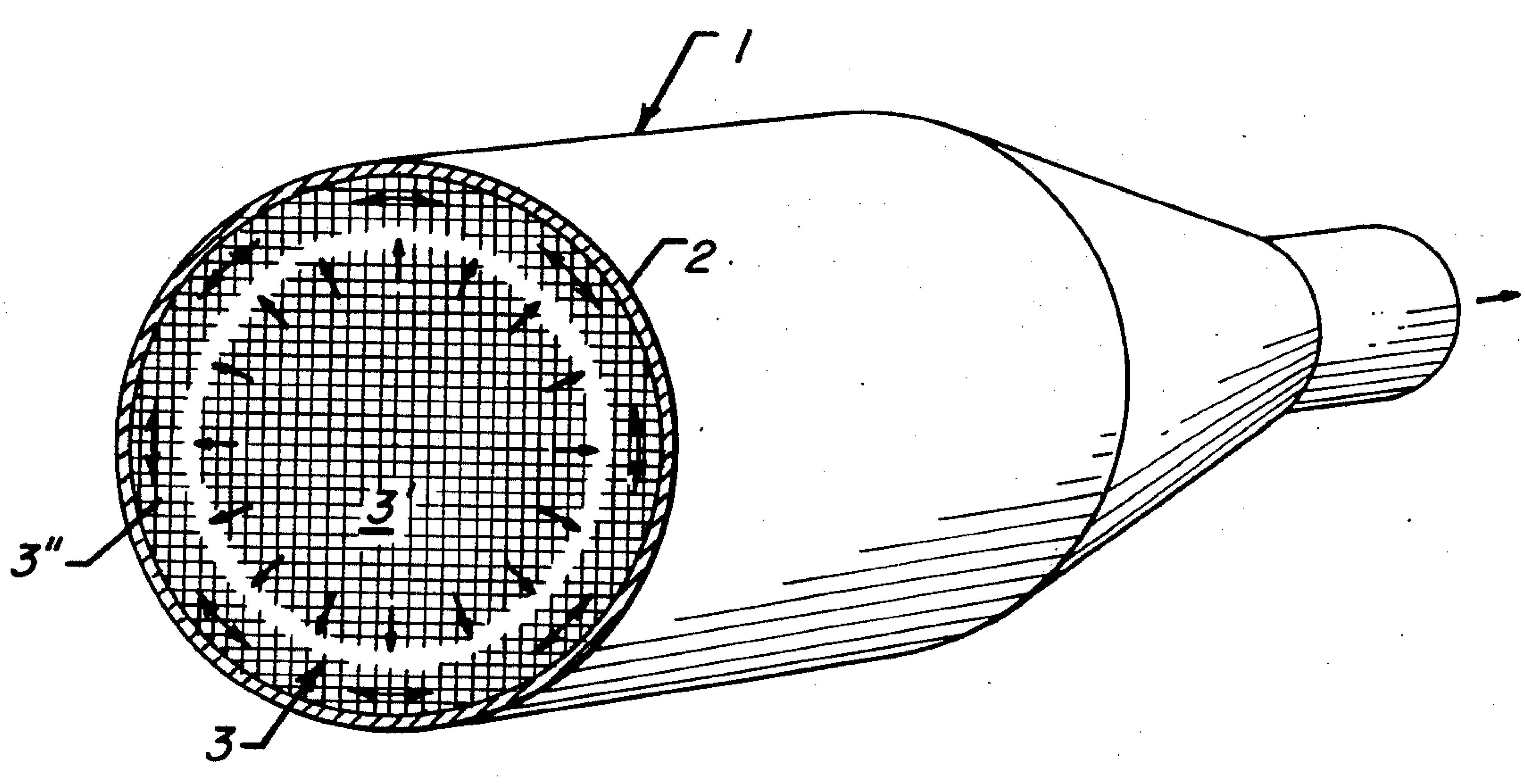

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Figure 1

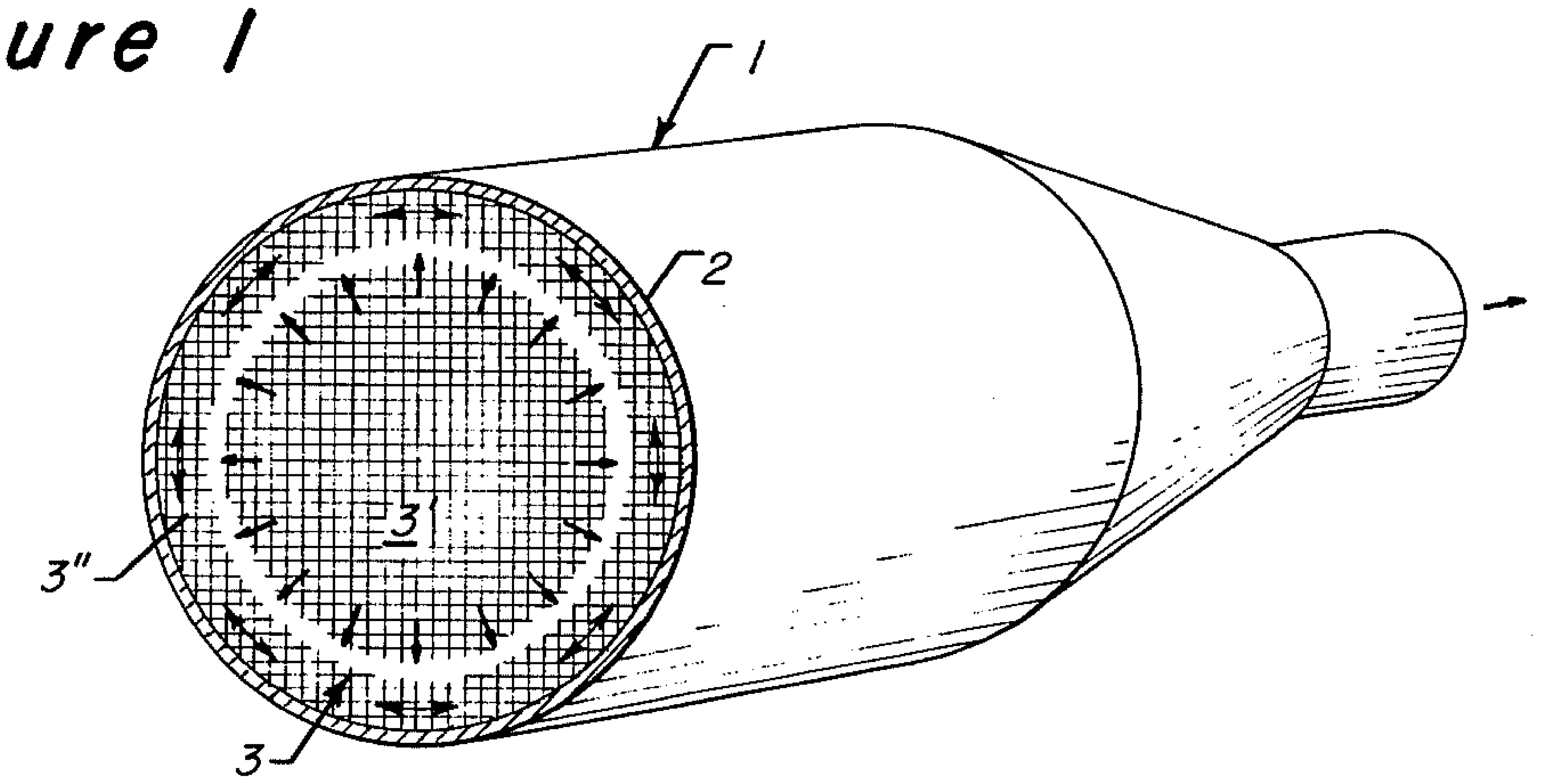


Figure 2

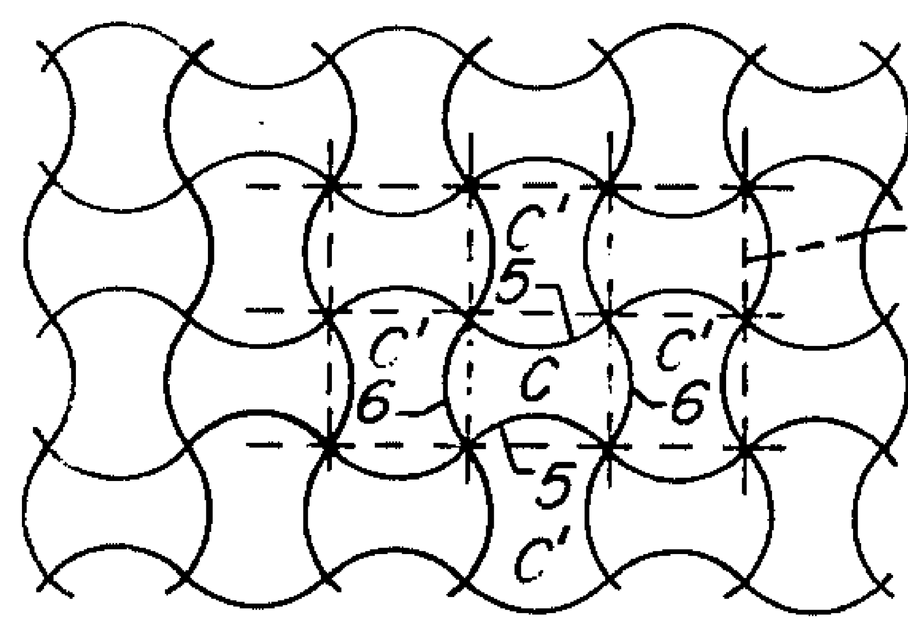
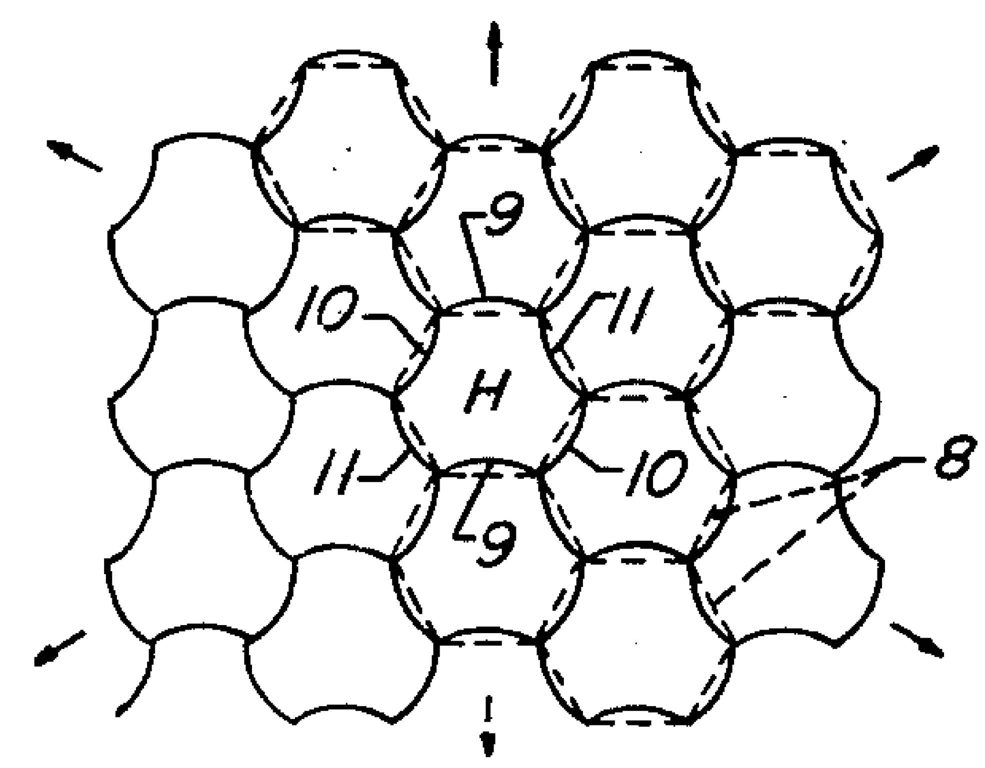


Figure 3



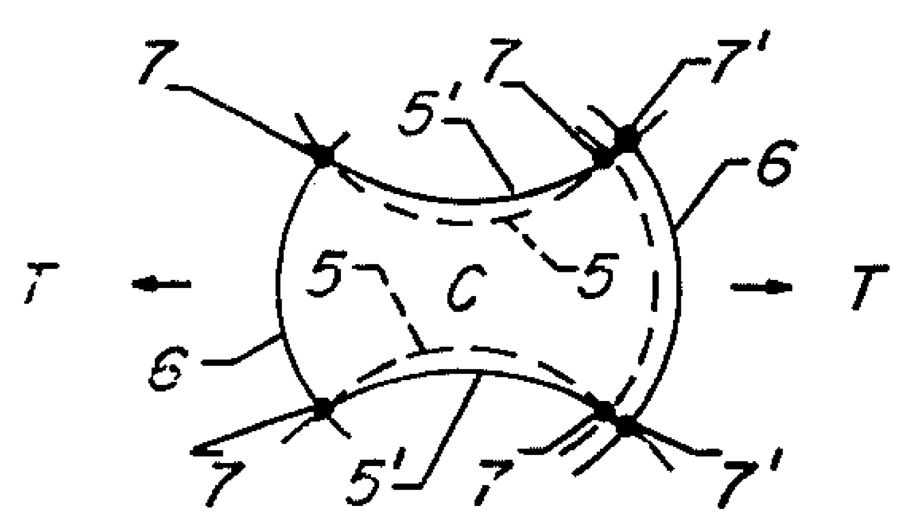


Figure 2A

Figure 4

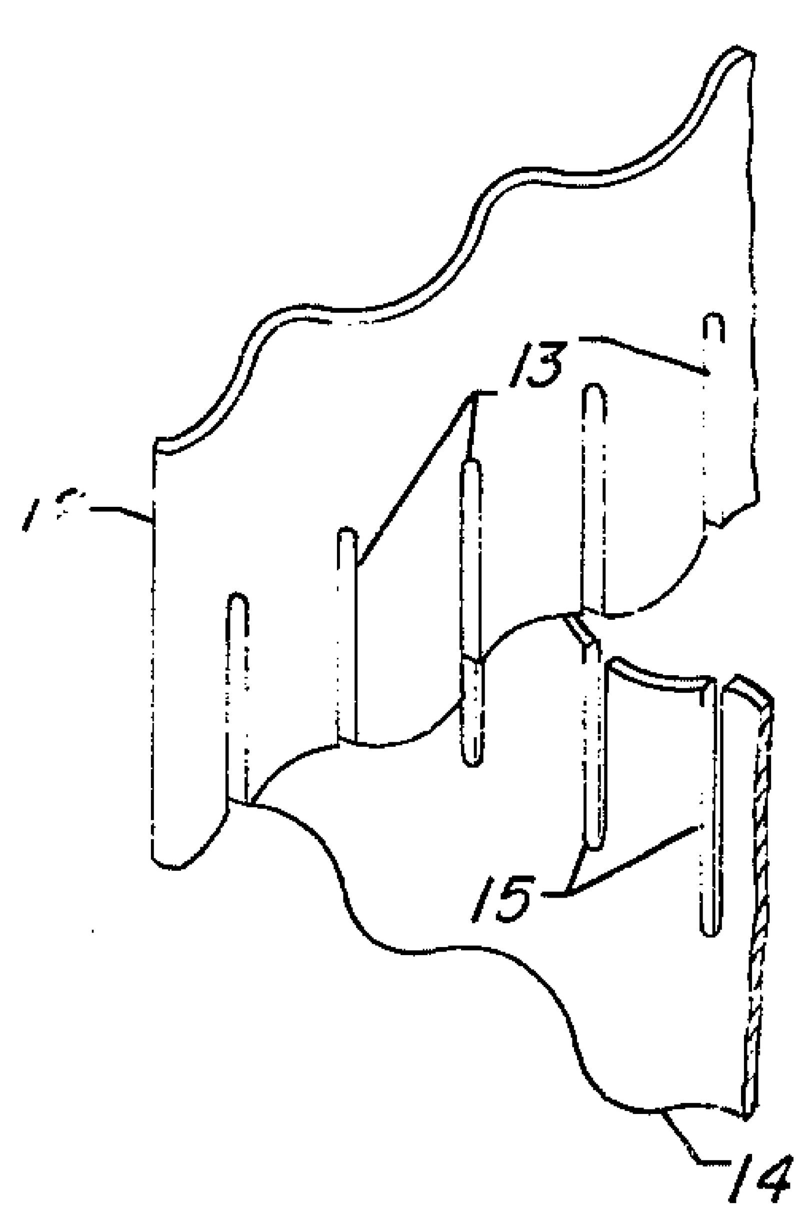
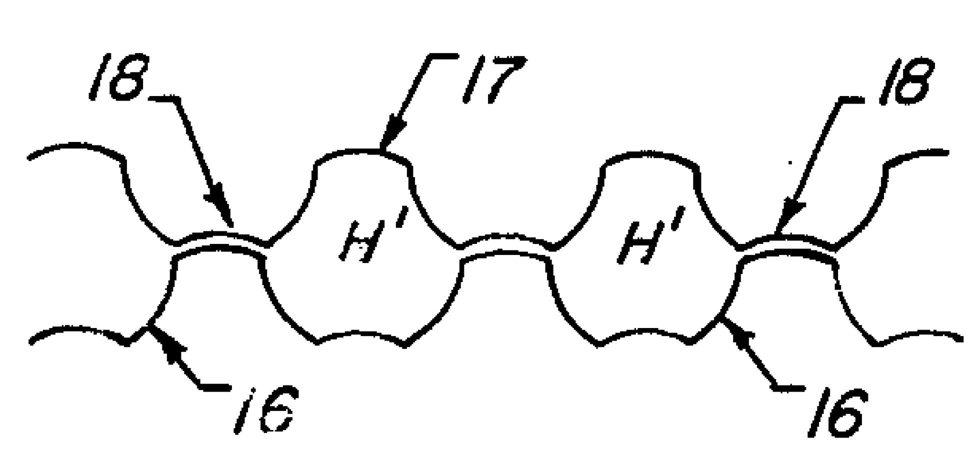


Figure 5



CERAMIC HONEYCOMB STRUCTURE FOR ACCOMMODATING COMPRESSION AND TENSION FORCES

The present invention relates to an improved design and arrangement for cells in a ceramic honeycomb structure such that there can be greater ability to withstand the compression and tension forces which can result from non-uniform high temperature conditions, as for example, when a honeycomb section is being utilized as a support for an oxidizing catalyst coating.

More particularly, there are herewith provided improved forms of honeycomb structures by virtue of special cell configurations which have all curved walls between common juncture lines forming the multiplicity of cells such that tension conditions can be better accommodated without causing breakage of the monolith walls.

One of the serious problems in connection with the use of ceramic monoliths or "honeycomb" type of structures as supports for catalyst coatings results from the fact that a catalyst structure, or even a bed of catalyst particulates, does not operate at a uniform temperature throughout its length or across its cross-section. There are normally substantial temperature differences between the inlet of the unit and the outlet end thereof, as well as differences between the central section and the areas adjacent to the catalyst chamber walls. As a result those sections of the catalyst unit which are at a higher temperature will undergo greater expansion than those at the lower temperatures and there will also be various sections of the monolithic unit undergoing either tension or compression. Typically, the ceramic composites forming the conventional forms of monoliths are fairly strong in compression, at least in comparison to tensile strength, such that there can readily be cracks and failures in the tensioned portions of a unit because of excessive stressing.

It is realized that various honeycomb configurations, with respect to the cross-section of cells, have been made and used for absorption elements and for catalyst supports in the air pollution field. Individual cells of a particular honeycomb may be square, rectangular, triangular, hexagonal, round, oval, etc., as well as of different sizes and diameters. Typically, where a ceramic honeycomb is used as a catalyst support member, it will be selected to have as small cells as possible, without creating excessive pressure drop for the fume stream, in order to provide a maximum of catalytic surface area. However, the smaller the cells, the greater is the rigidity and there is a lowering of flexibility for a given structure.

While it is a feature of the present invention to provide for curved interconnecting walls to extend between juncture lines and to effect the partitioning between adjacent parallel cells in a monolith, it must be realized that conventional circular or oval patterns for cells will not provide the desired flexure and deformation to help overcome tension breaks. Also, the curved wall cell configurations resulting from node to node contact points with the use of adjacent corrugated sheet manufacturing procedures, such as taught in U.S. Pat. No. 3,444,925, do not seem to result in suitable stress relieving patterns. For example, with a pattern providing circles, or ovals, in the cross-section of a honeycomb, there will be tensile forces without the available wall members to readily give and lengthen. Stated another way, with the use of curved wall patterns, from

circular or oval cells, there will still be a tendency for juncture lines to move closer together in a direction transverse to a tension force and there is no real elimination of breakage problems from non-uniform temperature conditions.

On the other hand, it may be considered a principal feature of the present invention to use curved members, rather than straight, to provide cell walls and connect juncture lines between a plurality of adjacent cells and, at the same time, have the curved walls form special patterns which will not tend to cause juncture lines to move closer together in a direction generally transverse to the walls being subjected to lengthening and straightening from a tensile condition.

The improved form of cell configuration can be accomplished, by way of example, in a design where square cells would have the straight walls replaced by arcs in which the curvature alternates between concave inward and convex outward to result in "dumb-bell" shaped cells. Also, where the walls of what would be a normal hexagonal pattern are made to be arcuate and they alternate between being concave inwardly and convex outwardly, then there is a resulting "cloverleaf" shape for each cell.

In a broad embodiment, the present invention provides a ceramic composite with a multiplicity of parallel cells in a honeycomb type of structure which can deform to accommodate compression and tensile forces from non-uniform temperature conditions, which comprises, having all interconnecting walls between juncture lines between adjacent cells being curved and oriented one to another in a reoccurring symmetrical pattern, with next adjacent walls around an individual cell alternately bowing inwardly and outwardly, and there being at least two sets of opposing curved walls to form each cell of said structure, whereby expansion movements in directions transverse to the length of the longitudinal cells that are due to differential temperature conditions can cause deformation and straightening of one set of opposing curved walls without causing juncture lines between cells to tend to move closer together in a direction generally transverse to the walls being straightened and to thereby provide a less fragile structure.

In a specific embodiment, there may be a configuration which is a modification of a conventional square pattern in that each cell will have an opposing set of partitioning walls which are concave toward one another and then at 90° thereto there will be a second set of partitioning walls which are curved outwardly, or convexly away from one another, such that the resulting configuration for each cell will be of a dumb-bell shape. Also, where walls alternate between bending inwardly and outwardly, the resulting overall pattern is such that any one cell will have adjoining dumb-bell shaped cell configurations that are at right angles thereto. This arrangement permits tensile stress elongation in one direction by virtue of wall curvature permitting some measure of desired elongation without breakage while, at the same time, there should be substantially no narrowing of spacing with respect to juncture points between cells in a direction transverse to the elongation. Actually, there may be some local spreading of juncture lines due to rotation thereof and to partial straightening of the transverse walls.

In another embodiment, there may be provided a curved wall modification for what might normally be considered a hexagonal cell pattern, with three sets of opposing curved walls rather than three sets of straight walls as provided in a conventional hexagon. Opposing curved partitioning walls between adjacent cells in any one row thereof will be bowed in the same direction and each cell in any given row of cells will have the same cross-sectional configuration and orientation. Also in this arrangement, the curved walls for any one cell will alternate between being concave inwardly and convex outwardly around the periphery of such cell such that the result is a cell unit being generally of clover-leaf shape. With respect to flexibility, this arrangement permits tensile forces to, in effect, straighten or elongate two sets of wall portions of a particular cell with little or no movement between juncture lines in a direction transverse to the tensile forces, whereby flexibility is in effect built into the honeycomb structure to accommodate differential temperature conditions. The deformation and flexibility aspects will be more clearly explained and set forth in connection with the subsequent description of the drawings.

The desired special cell configurations in a honeycomb type of structure may be obtained during the manufacturing process by extruding the ceramic material through suitably shaped die means; however, other forms of manufacture may be utilized. For example, specially shaped modifications of a corrugated type sheet may be utilized to conform with and form a juncture with other specially formed sheet members such that the desired clover-leaf pattern could result in the final product. In other words, the procedure of manufacturing honeycomb type of monolithic structures such as set forth in U.S. Pat. Nos. 3,444,925 and 3,505,030 might well be utilized in the present instance. Also, sheet-like members of ceramic material in a curved or corrugated form may be slotted and subsequently nested in the manner of making an egg-crate type of carton to form the modified, curved wall square, configuration where the result is the multiplicity of dumb-cell shaped cells. Where sheets of corrugated films of green ceramic are nested with, or made to contact adjacent sheets or panels, then during the curing or firing stage there is a fusing and sintering of the contacting sheets to form the desired shapes and juncture points between longitudinal cells, such as is set forth and described in the aforementioned patents.

In still another procedure, there can be the formation of a ceramic mixture around suitably shaped burnable core members and a firing and burning away of the core material from the ceramic material to result in desired shaped cells for the honeycomb element. In other words, it is not intended to limit the present invention to any one method of making the honeycomb ceramic structure, nor is it intended to limit the invention to any one type of material that will form the resulting rigid cellular structure. For example, the ceramic may comprise refractory crystalline materials such as sillimanite, magnesium silicates, zircon, petalite, spodumene, cordierite, alumino-silicates, mullite, etc. Such materials are of advantage in having relatively high porosity over their surface areas and being suitable for supporting catalyst coatings to, in turn, provide catalytically active conversion elements.

The present honeycomb elements may be utilized to advantage, without catalyst coatings, as absorption structures or heat exchange elements; however, such types of coated structures are finding wide usage in catalytic converters adapted to have auto exhaust fumes passed therethrough to effect conversion and elimination of undesired components such as carbon monoxide, hydrocarbons and nitrogen oxides. While it is not intended to limit the present invention to any one specific type of active catalyst coating, such coating may comprise an oxidation catalyst and may include the metals of Groups I, V, VI and VIII of the Periodic Table, particularly copper, silver, vanadium, chromium, iron, cobalt, nickel, platinum, palladium, with a component being used singly or in combination with one or more other active component. Also, typically, the ceramic honeycomb material will have been coated with a suitable refractory inorganic oxide such as alumina or alumina combined with one or more other refractory inorganic oxide. Typically, the oxide supporting layer will be applied to the wall surface prior to the coating of the active catalytic component although there may be a mixture of refractory metal oxide support material with the active catalytic component and the mixture sprayed, dipped or otherwise coated onto the walls of the cellular structure. Although not intended to be limiting, reference may be made to U.S. Pat. No. 3,565,830, which sets forth various methods for coating a refractory honeycomb type of member with an alumina slip and an active catalytic coating.

Reference to the accompanying drawing and the following description thereof will serve to illustrate variations in the flexible cell design being provided for a honeycomb type of ceramic structure and the means for forming the special cell configurations, as well as point out how differential temperature conditions provide failure problems with conventional ceramic honeycomb elements.

FIG. **1** of the drawing indicates diagrammatically how differential temperature conditions across a conventional honeycomb element can create tensile forces leading to breakage in cell walls of a honeycomb element.

FIGS. **2** and **3** of the drawing indicate diagrammatically two different forms of cellular configurations which provide curved wall portions that can better accommodate tensile stressing from differential temperature conditions.

FIG. **2A** indicates diagrammatically how an individual cell may be deformed and elongated without leading to immediate breakage.

FIGS. **4** and **5** indicate diagrammatically how specially formed ceramic sheet material may be joined with other specially formed sheets to provide resulting curved wall cells.

Referring now particularly to FIG. **1** of the drawing, there is indicated a portion of reactor unit **1** having a cylindrical form wall or chamber portion **2** adapted to hold an internal honeycomb element **3**. Where the unit is serving as an exhaust fume reactor to convert hydrocarbon containing exhaust gas fumes and the cellular structure **3** is catalytically coated with an active oxidation catalyst, there can be high temperature conditions through the interior of the reactor of the order of 1200° to 1600° F. However, during certain stages of operation and perhaps during most operating periods, there will be a substantially higher temperature in the central core portion **3'** as compared to the peripheral portion of the honeycomb, being indicated as **3''**. The hot interior will therefore tend to expand, from the high temperature conditions, to a far greater degree than the peripheral section 3'' and, as indicated by the arrows, the outward thrust from the expansion of the interior material will necessarily cause resulting hoop stress or tension in the outer ring of cells 3'' and lead to wall breakage. As indicated hereinbefore, typical ceramic materials can be relatively strong under compression conditions but will have very little strength to accommodate tensile forces and will readily shatter and break, particularly where straight walls are being utilized for the honeycomb cell configuration such as indicated in the present FIG. **1**.

With reference to FIG. **2** of the drawing, there is indicated a special cell configuration which provides curved wall portions that can, in turn, provide flexure to a resulting honeycomb element. Specifically, there is indicated a curved wall modification for what might be considered a normally square pattern or layout such as indicated by the dashed lines **4**. In particular, the present pattern is provided by having all arced or curved walls for each and every cell of the entire honeycomb structure with the curved walls alternating around a particular cell from being curved inwardly to being curved outwardly. With reference to a particular cell such as C, it will be noted that there are opposing walls **5** which are concave toward one another while at right angles thereto there are opposing walls **6** that are convex outwardly to bow away from one another. The net result is a dumb-bell type of shape for the cell C by virtue of the necked-in portion in the central zone. It will also be noted that the pattern for C is repeated at every other location in any one row. It may also be noted that each next adjacent, or touching, cell c' has the same dumb-bell configuration but is at right angles to C in orientation.

In order to further illustrate the flexibility or deformation characteristic for each cell, reference may be made to FIG. **2A** of the drawing, where an individual cell C is bounded by juncture lines **7** and walls **5** and **6**; however, when tensile forces T are exerted with respect to the walls of the cell in the direction indicated, there can be straightening of the walls **5** into the partially flattened shapes **5'** and the displacement of juncture lines **7** into positionings **7'** without causing juncture lines **7** to move closer to one another. In other words, the curved or arcuate walls **5** will tend to deform into a somewhat straighter configuration without necessarily causing immediate breakage to permit juncture lines to shift somewhat and give overall flexibility to the unitary honeycomb structure. Actually, there is probably some rotation of the immediate juncture lines at **7** and **7'** due to rigidity and moment forces that could cause some straightening of walls **6** and a slight spreading apart of junctures **7** and **7'**.

In FIG. **3** of the drawing, there is indicated what might be considered a modified hexagonal cell pattern where hexagonal cells, indicated by dash lines **8**, are provided with alternating curved wall portions to result in a modified clover-leaf pattern. Specifically, each cell H has an opposing set of walls **9** that curve or bow in the same direction in any one line of cells, another opposing set of walls **10** which also bow in the same direction in their row, and a third set of opposing walls **11** which bow in the same direction in their row. It will also be noted that there is the alternate bowing outwardly and inwardly with respect to next adjacent walls around the periphery of the cell H, with one wall **9** going outwardly and the next adjacent walls **10** and **11** bowing inwardly or, conversely, where a wall **9** bows inwardly the next adjacent walls **10** and **11** will bow outwardly. In this clover-leaf pattern, each cell H in any one row along any one of the three rows thereof, that are 120° apart, will have the same pattern or configuration.

It may be noted further with respect to FIG. **3** of the drawing, as compared to the pattern in FIG. **2**, that the three sets of opposing walls for any one cell will permit tensile forces to act along more than one direction at the same time and that normally four wall sections will be tending to flatten or straighten out under tensile forces and that four juncture lines may be displaced with respect to any one cell along the direction of the tensile forces. Still further, juncture lines in a transverse direction to the tensile forces will not tend to move toward one another and will be maintained separate by rotational effects at juncture lines and by the compressive resistance of the opposing walls which are extending generally transverse to the direction of the tensile forces. Again, the net result is that the curved wall portions can resist tensile forces by being deformed and flattened to some degree while at the same time permit juncture lines to move and be displaced within any one honeycomb structure in a manner so as to eliminate breakage of individual wall members and a resulting failure to the overall ceramic structure.

In FIG. **4** of the drawing there is indicated a manufacturing procedure when corrugated shaped partitioning members of green ceramic may be intermeshed at substantially right angles to one another to form intersecting and adjacent wall portions of a cell, and whereby a plurality of such members can result in a configuration similar to that shown in FIG. **2** of the drawing. Specifically, a plurality of corrugated form members, such as **12** with slots **13**, can be made to fit "egg crate" fashion into a plurality of corrugated members, such as **14** having slots **15**, and at 90° thereto to form a cellular type of structure. It is to be realized that any number of wall members **12** at desired spaced distances would be utilized in one direction to fit into the spaced slots **15** and that another plurality of wall members **14** would be utilized at desired parallel spaced distances from one another to fit into the slots **13** such that there is the intermeshing of the walls to result in the configuration of FIG. **2** with desired sized cells. A heating and curing operation following the interlocking of members will result in the desired sintering of the wall members to form tightly fused juncture lines between resulting parallel cells throughout the honeycomb structure.

In FIG. **5** of the drawing, there is indicated that a specially formed green sheet of ceramic material, such as **16**, can be brought into contact with a next adjacent specially formed sheet **17** at the arcuate zones **18** to result in cell patterns H' and that such system might well be utilized to form a cellular structure with a multiplicity of cells H'. The heating and fusing of the juncture areas **18** will provide the sintering and "welding" of all of the sheets into a resulting rigid structure.

Although the desired cell patterns and configurations may be obtained in accordance with the procedures set forth in connection with the descriptions of FIGS. **4** and **5**, it is generally preferred that the desired cell patterns be obtained by an extruding procedure where accurate uniform, thin wall partitions can be provided between the multiplicity of specially shaped cells in any one structure.

The size of the cells in a particular honeycomb structure, as hereinbefore noted, will typically be selected to be in accordance with pressure drop limitations for a particular stream being passed through a honeycomb element, or through a series of elements. Typically, cell sizes may be from one thirty-second inch, or less, nominal diameter to one-half inch or more. It may also be noted that honeycomb elements may be of varying shapes for a particular reactor chamber or housing and that special shapes may be cut from larger honeycomb units produced under any one form of manufacturing procedure.

The present forms or configurations of cellular structures may be made to have varying coefficients of expansion depending upon the type of ceramic material utilized in manufacturing the skeletal honeycomb material. Typically, the coefficient of expansion for the honeycomb structure will be small as compared to steel or other metal housings and as a result a core element of the present invention may well be utilized in metal housings without requiring a resilient expansion absorbing medium between the external wall of the honeycomb structure and the inside wall of the housing. In other words, honeycomb materials utilizing the present forms of configurations can have a certain degree of flexibility within the housing without undergoing breakage problems when subjected to non-uniform temperature conditions.

I claim as my invention:

1. A ceramic composite with a multiplicity of parallel cells in a honeycomb type of structure which can deform to accommodate compression and tensile forces from non-uniform temperature conditions, which comprises, having all interconnecting walls between juncture lines of the walls and between adjacent cells being curved and oriented one to another in a reoccurring symmetrical pattern, each of said parallel cells being formed and defined by two sets of opposing curved walls, and with one set of walls generally normal to the other in the overall pattern and at the junctures, said walls for any one cell being such that one set of opposing walls will bow towards one another and the other set will bow away from one another to form a necked-in and dumb-bell form of cross-sectional configuration, and all cells having a common wall with an adjacent cell will be of the same configuration as such cell except that it will be in an orientation of 90° with respect thereto, whereby expansion movements in directions transverse to the length of the longitudinal cells that are due to differential temperature conditions can cause deformation and straightening of one set of opposing curved walls without causing juncture lines between cells to tend to move closer together in a direction generally transverse to the walls being straightened and to thereby provide a less fragile structure.

2. The ceramic composite structure claim **1** further characterized in that said structure is provided with an active oxidizing catalyst coating material suitable to provide for the conversion of a noxious-gaseous stream.

3. A ceramic composite with a multiplicity of parallel cells in a honeycomb type of structure which can deform to accommodate compression and tensile forces from non-uniform temperature conditions, which comprises, having all interconnecting walls between juncture lines of the walls and between adjacent cells being curved and oriented one to another in a reoccurring symmetrical pattern, each of said parallel cells being formed and defined by three sets of opposing curved walls, with each set of walls being at approximately 120° with respect to the next adjacent set of walls to define any one cell, with next adjacent walls around an individual cell alternately bowing inwardly and outwardly, opposing curved partitioning walls between adjacent cells in any one row thereof are bowed in the same direction, and each cell in any given row of cells has the same cross-sectional configuration as the other cells and is in the same orientation, whereby to readily provide tension and deformation along any one of three axis without causing any substantial reduced spacing between juncture lines along either of the other 120° transverse axes.

4. The ceramic composite structure of claim **3** further characterized in that said structure is provided with an active oxidizing catalyst coating material suitable to provide for the conversion of a noxious gaseous stream.

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