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 [31] **46500/67**

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[54] **METHOD AND APPARATUS FOR ELECTRICALLY HEATING A FLUID**
29 Claims, 7 Drawing Figs.

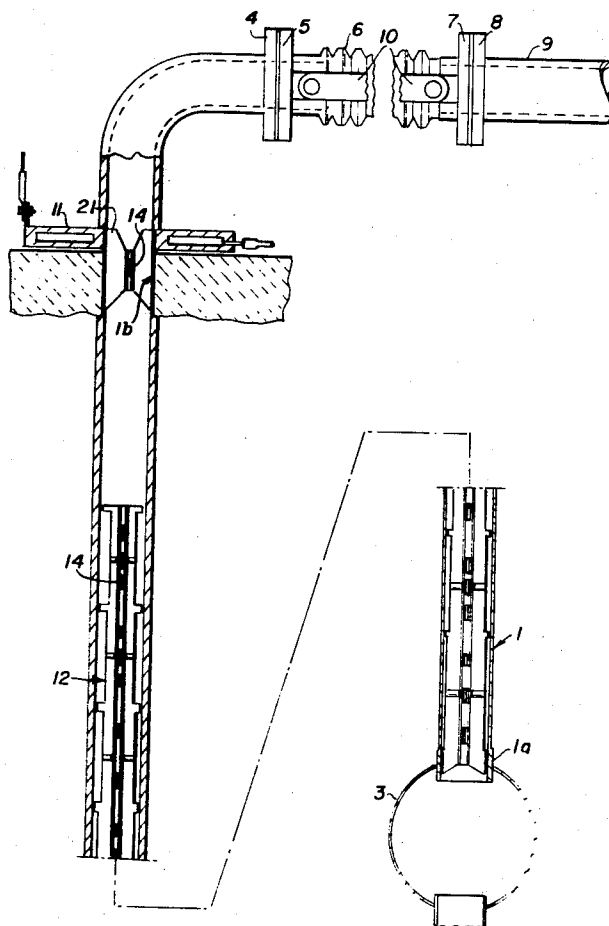
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H05b 1/00
 [50] Field of Search..... **219/296,**
300-305, 298; 23/202, 277 R

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ABSTRACT: A process and apparatus for heating fluids, particularly gaseous halides of titanium, silicon, aluminum, zirconium and mixtures thereof. The fluid to be heated is passed through at least one metal tube which has a plurality of metal fins disposed internally of said tube, the fins being in electrical contact with the wall of the tube. An electrical potential is applied between two points spaced apart along the length of the tube to cause an electric current to flow through the wall of said tube and said fins to thereby heat the tube wall and the fins. The configuration of said tube wall and said fins is such that the cross-sectional area of the flow path of the electric current between the said two points increases in the direction of flow of the gas in said tube to thereby prevent the temperature of the inner surface of the wall of the tube from increasing in the direction of flow of said fluid. In addition, the configuration of the fins is such that the temperature of the surface of the fins that are exposed to the fluid does not substantially exceed the maximum temperature of the inner surface of the wall of the tube between said two points.



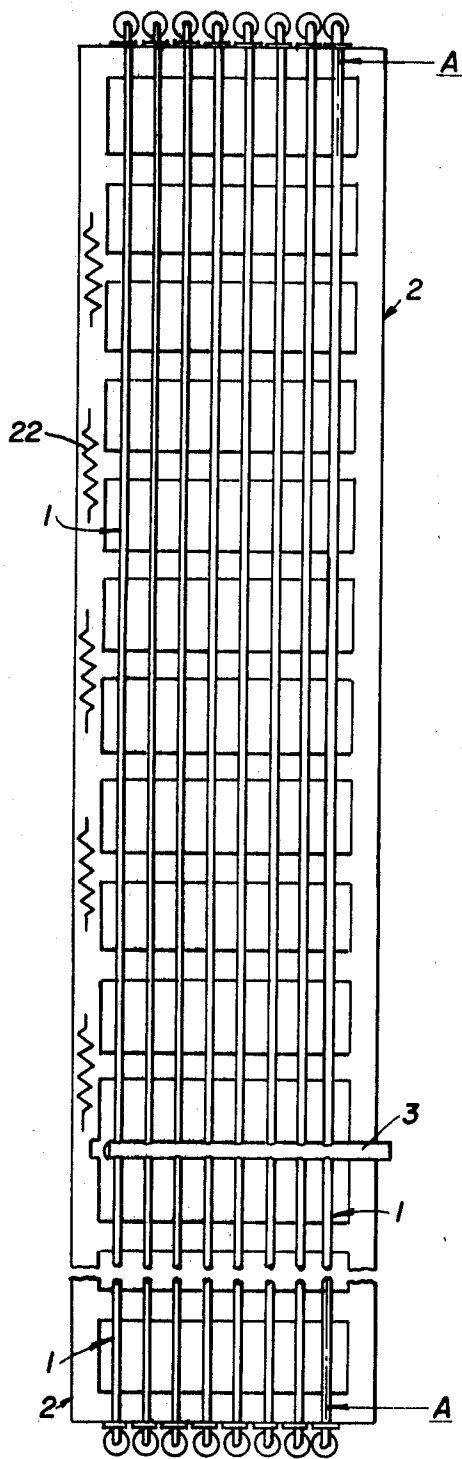


FIG. 1

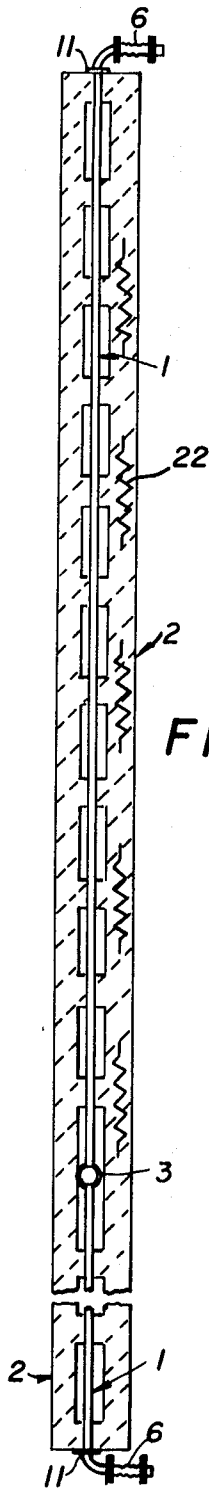


FIG. 2

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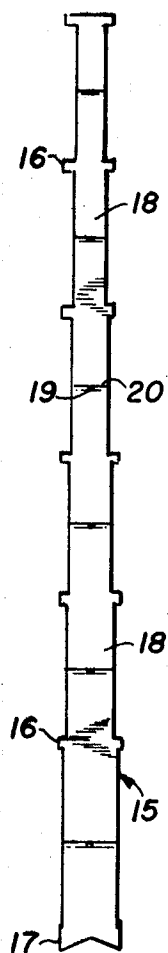


FIG. 4

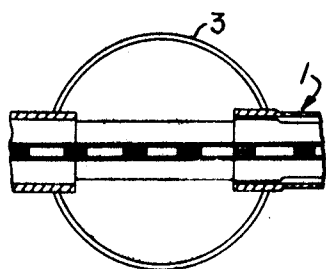


FIG. 7

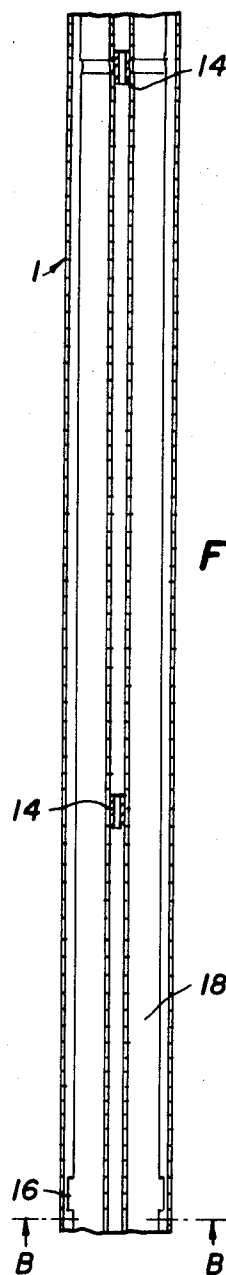


FIG. 5

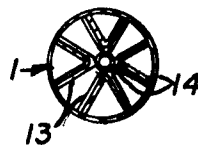


FIG. 6

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METHOD AND APPARATUS FOR ELECTRICALLY HEATING A FLUID

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the heating of fluids. More particularly, the invention relates to a process and apparatus for heating gaseous halides (excluding the fluoride) of titanium, silicon, aluminum, zirconium and mixtures thereof.

2. Description of the Prior Art

It is known to heat a fluid by passing it through a heated metal tube. However, a problem may arise because of an inherent requirement that the apparatus must be light or because of economic considerations, such as when it is necessary to construct the tube of an expensive metal.

Thus, for example, it is known to heat vapors of halides of titanium, silicon, aluminum, zirconium and mixtures thereof to relatively high temperatures of the order of 700° C. to 1,100° C., for example, for the purpose of bringing them up to the temperature necessary to enable them to undergo oxidation reactions with oxidizing gases. However, the heating of such halide vapors presents a number of problems because of the corrosive nature of the halides at such temperatures. It has been suggested heretofore to use platinum or a suitable alloy thereof as the material of construction for portions of the apparatus that are exposed to the hot halide vapors to thereby reduce the rate of corrosion to an acceptable level. However, the high cost of platinum and its alloys is a disadvantage in such a construction.

The present invention permits a reduction in the amount of metal required in such a heating process and apparatus.

SUMMARY OF THE INVENTION

The present invention provides a process for heating a fluid which comprises, passing the fluid through at least one metal tube that is provided internally with metal fins or other members arranged to increase the area of contact with the fluid and which are in electrical contact with the wall of the tube, and heating the wall of the tube and the fins or other members by applying an electrical potential difference between two points spaced apart along the length of the tube to thereby cause an electric current to flow through both the wall of the tube and said fins. The configuration of said tube wall and said fins is such that the cross-sectional area of the flow path of the electric current between the said two points increases, at least over a length of the tube immediately upstream of the downstream one of the said two points, in the direction of flow of the fluid in such manner as to tend to prevent the temperature of the inner surface of the wall of the tube from increasing in the direction of flow of the fluid. In addition, the configuration of the fins is such that the temperature of their surfaces that are exposed to the fluid nowhere substantially exceeds the maximum temperature of the inner surface of the wall of the tube between the said two points.

The invention also provides apparatus for heating a fluid, which comprises at least one metal tube through which the fluid can be passed, fins or other members provided internally of said tube, said fins being arranged to increase the area of contact with the fluid and being in electrical contact with the wall of said tube, and means for applying an electrical potential difference between two points spaced apart along the length of the tube to cause an electrical current to flow through the wall of the tube and said fins and thereby heat said wall and said fins. The configuration of the tube wall and of the fins is such that the total cross-sectional area of said tube wall and said fins increases along the tube in one direction in such manner that when the fluid is caused to flow through the tube in the direction in which the said cross-sectional area increases and the tube and fins are heated by applying an electrical potential difference between said two points, the said increase in cross-sectional area tends to prevent the temperature of the inner surface of the wall of the tube that is exposed to the fluid from increasing in the direction of flow of the fluid,

at least over a length of the tube immediately upstream of the downstream one of the said two points. The temperature of the surfaces of the fins that are exposed to the fluid nowhere substantially exceeds the maximum temperature of the inner surface of the tube between the said two points.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic plan view of one embodiment of the apparatus of this invention, with the upper wall of the enclosure removed;

FIG. 2 is a diagrammatic sectional view taken on the line A—A in FIG. 1;

FIG. 3 is a diagrammatic longitudinal vertical section, not to scale, taken through one of the tubes and associated equipment;

FIG. 4 is a plan view, also not to scale, of one pair of fins opened out flat;

FIG. 5 is an axial section taken through a short, length of one of the tubes on a larger scale; and

FIG. 6 is a cross-sectional view taken on the line B—B of FIG. 5.

FIG. 7 is a diagrammatic longitudinal vertical section, not to scale, showing a further embodiment of the juncture of the tubes and the outlet conduit shown in FIG. 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, there is provided a process and apparatus for heating a fluid to a relatively high temperature. As noted hereinabove, the apparatus of this invention comprises at least one metal tubular member through which a fluid to be heated can be passed, with the tubular member being provided internally with fins or other members which extend over a substantial length of the tube. The fins are arranged within the tubular member to increase the area of contact with the fluid passed through the tube and are in electrical contact with the wall of the tubular member. Means are provided for applying an electrical potential between two points spaced along the length of the tube to cause an electrical current to flow through the wall of the tube and the fins and thereby heat said wall and said fins. The tube and the fins must, of course, be formed of a metal which is electrically conductive.

According to the present invention, the configuration of the wall of the tube and of the fins is such that the total cross-sectional area of said wall and said fins increases along the tube in the direction in which the fluid is passed through the tube. Such a configuration prevents the temperature of the wall of the tubular member from increasing in the direction of flow of the gas in the tube and thereby provides a substantially uniform temperature distribution over the length of the tube.

This invention makes it possible to reduce the quantity of metal as compared with the use of a plain tubular preheater in which the tubes are heated by radiation from the walls of a furnace within which the tubes are situated. Neglecting variations in the thickness of the wall of the tube (and a certain minimum wall thickness is required to give adequate structural strength), minimization of the weight of metal requires that all the metal shall be at as high a temperature as possible. Since corrosion, mechanical strength requirements and other considerations place an upper limit on the maximum temperature of the metal, the requirement that the temperature of the metal shall be as high as possible implies that the temperature shall be as uniform as possible.

The invention also makes it possible to achieve a more uniform temperature distribution of the metal in two ways. First, at the end of the tube where the fluid is cooler, the use of electric resistance heating of this invention within the metal itself makes it possible to achieve heat input rates that, owing to the relatively low radiant absorptivity of most metals (especially platinum, the alloys thereof mentioned hereinafter and certain other metals), could only be achieved by radiation with the use of impracticably high furnace wall temperatures

when the tube is heated by radiation. Secondly, the increase in the cross-sectional area of the flow path of the electric current towards the end of the tube where the fluid is hotter, implies a corresponding reduction in the rate of generation of heat per unit length of the tube in that direction. Such a reduction permits the use of current densities at the upstream end of the tube that would otherwise lead to overheating at the downstream end of the tube by tending to compensate for the reduction in the cooling effect of the fluid as its temperature rises.

If a plain tube, that is, a tube of uniform diameter and wall thickness not provided with fins or other members, as in the present invention, is heated by passing an electric current through it, and taken as the basis for comparison (instead of a plain tube heated by radiation), the advantage afforded by the invention is even greater. This is due to the fact that when the tube is heated by radiation, there is a greater heat input to the tube at the relatively cold upstream end than at the relatively hot downstream end (which tends to compensate to some extent for the greater cooling effect of the fluid at the upstream end) whereas, when the tube is heated by passing an electric current through it, the rate of input of heat is uniform along the length of the tube. Thus, for a given input temperature of the fluid and a given maximum temperature of the metal, the length of plain tube required to raise the temperature of the fluid to a given value will be less when the tube is heated by radiation than when the tube is heated by passing an electric current through it, assuming that other variables, principally, the mass flow rate of the fluid and the diameter of the tube, are the same in each case. It is surprising that, by providing the tube with internal fins and heating the tube and the fins by passing an electric current through them in accordance with this invention, the tube cannot only be shortened even as compared with the radiantly heated plain tube, but can be shortened more than sufficiently to compensate for the quantity of metal used to form the fins.

It will be apparent that in order to prevent local overheating of surfaces that are exposed to the fluid, or unduly restricting the magnitude of the electric current, the said total cross-sectional area of the flow path of the electric current between the two said points must, for given values of the electric current and the mass flow rate of the fluid, substantially everywhere exceed some function of distance along the tube, measured from the upstream one of the said two points, that increases with distance in the downstream direction. At the same line, in order that the surfaces that are exposed to the fluid shall reach a sufficiently high temperature to keep the total quantity of metal required below a given value, the said total cross-sectional area should be less than some other such increasing function of distance along the tube over most of the distance between the said two points. The minimum value of the latter function between the said two points is less than the maximum value of the former function between the said two points. While a small region of reduced total cross-sectional area (as compared with the said total cross-sectional areas immediately upstream and downstream of the said small region) generally necessitates restricting the magnitude of the electric current if local overheating is to be avoided, small regions of increased total cross-sectional area merely result in a correspondingly small increase in the total quantity of metal required. This may be acceptable if, for example, the provision of such small regions of increased total cross-sectional area facilitates the mounting of the fins within the tube.

The advantages afforded by the invention are especially pronounced when the fluid is the vapor of a halide (excluding the fluoride) of one of the elements titanium, silicon, aluminum, and zirconium, or a mixture of more than one of such halides, and at least the surfaces of the tubes and of the fins or other members that are exposed to the halide vapor are formed of platinum or an alloy of platinum with rhodium, ruthenium or iridium.

The heating of such halide vapors up to relatively high temperatures of the order of 700° C. to 1,100° C., for the purpose

for example, of bringing them up to temperatures at which they will undergo oxidation reactions with oxidizing gases, presents problems because of the corrosive nature of the halides at such temperatures. The use of platinum or a suitable alloy thereof as the material of construction for portions of the apparatus that are exposed to the hot halide vapor makes it possible to reduce the rate of corrosion to an acceptable level, and the saving in platinum or platinum alloys that is made possible by the invention is of very considerable economic importance because of the high cost of these materials.

The fluid must not, of course, have a sufficiently high electrical conductivity to have any substantial effect on the magnitude of the electric current that flow through the wall of the tube and through the fins or other members.

The apparatus of this invention may comprise a single tube or a plurality of such tubes, each provided internally with fins or other members and being so interconnected as to enable fluid to be caused to flow through them in parallel.

The tube or tubes are advantageously situated in a thermally insulated region, for example, in an enclosure lined with a nonmetallic refractory material. In order to reduce heat losses from the tube or tubes, the wall of said thermally insulated region may, if desired, be heated other than by radiation from the tube or tubes. Preferably, however, the walls of said region are maintained at a temperature below the temperature of the outer surface of the tubes at the downstream one of said two points. This is due to the fact that the resulting net radiation loss from the tubes further increases the maximum current that can flow in the wall of the tube without overheating and thereby makes it possible to reduce still further the quantity of metal used. The optimum degree of cooling depends upon a balance between the saving on the weight of metal on the one hand and the increased consumption of electricity on the other hand.

The significance of maintaining the walls of the enclosure at a temperature below that of the outer surface of the tubes at the downstream one of the said two points can more readily be appreciated by considering apparatus that comprises a tube provided with internal fins formed (as is described hereinafter) from laminar material of the same thickness as the wall of the tube, the thickness of the wall being small by comparison with the diameter of the tube. Then, assuming that the tube and fins are constructed entirely of a single material and neglecting the effect of the free edges (if any) of the fins and the fact that the exposed area of the inner surface of the tube is reduced by the fins where they are secured to the tube, the surface area of the fins that is exposed to the fluid, per unit mass of fin, is twice the surface area of the wall that is exposed to the fluid, per unit mass of the wall. On the other hand, rate rate of generation of heat per unit mass of metal is the same for the fins and the wall of the tube. Thus, if the walls of the enclosure are maintained at the same temperature as the outer surface of the tube at some point along its length, so that there is no net heat loss from the tube at that point by radiation to the walls of the enclosure, the wall of the tube has to lose heat to the halide vapor at that point at a rate per unit area of exposed surface that is twice the corresponding rate for the fins at that point. This implies that, at the point in question, the temperature of the wall of the tube must be significantly higher than the temperature of the fins, so that the fins are below the optimum temperature and are therefore not operating at the maximum rate of heat output per unit mass of metal. When the point in question is at the downstream one of the said two points, where the fins are large and the mass of the fins per unit length of the tube may, in fact, be larger than the mass of the tube wall per unit length of the tube, this represents a considerable wastage of metal. Although the temperature of the fins can readily be increased merely by increasing their thickness while leaving their total cross-sectional area unchanged, this does not increase the rate of heat output per unit mass of metal of the fins and so does not result in any saving of metal. By arranging that the tube loses heat by radiation to the walls of the enclosure, on the other hand, it is

possible to save metal because fins of smaller cross-sectional area will then suffice to prevent the wall of the tube from exceeding the desired maximum temperature.

The flow rate of the fluid through the tube, the magnitude of the electric potential applied between the said two points and the configuration of the fins may be such that, for at least 50 percent and preferably at least 80 percent of its area between the said two points, the temperature of the inner surface of each tube that is exposed to the fluid is within 200° C. (advantageously, within 100° C. and preferably, within 50° C.) of the highest temperature at any point of the said inner surface that is exposed to the fluid. Also, the flow rate of the fluid through the tube, the magnitude of the electric potential applied between the said two points and the configuration of the fins are advantageously such that the temperature of the inner surface of each tube that is exposed to the fluid is within a range of about 300° C. and preferably within a range of about 150° C. everywhere between the said two points except in the immediate vicinity of the upstream point. Preferably, when the cross-sectional area of the wall of each tube is uniform between the said two points, the flow rate of the fluid through the tube, the magnitude of the electrical potential applied between the said two points and the configuration of the fins are such that the temperature distribution over the inner surface of each tube that is exposed to the fluid is substantially uniform between the said two points except in the immediate vicinity of the upstream point.

The configuration of the fins can vary widely. This is largely because the rate of generation of heat in the wall of a given short length of a tube is the same for all configurations of the fins in such a short length which have the same total cross-sectional area of the flow path of the electric current over the said short length. Thus, neglecting any effect that varying the configuration of the fins may have on the transfer of heat between the fin and the wall of the tube or on the flow of fluid through the tube, any variation in the configuration of the fins that leaves the said total cross-sectional area unchanged will also leave the temperature of the inner surface of the wall of the tube unchanged. In contrast to this, any variation in the configuration of the fins that results in an increase in the area that is exposed to the fluid per unit length of the tube, while leaving the said total cross-sectional area unchanged, will result in a decrease in the temperature of the fins themselves. Thus, in order to ensure that the fins do not themselves reach too high a temperature it is merely necessary to arrange that they have a sufficiently high surface area in relation to their cross-sectional area.

The fins are advantageously formed from laminar material and have both surfaces exposed to the fluid. The thickness of the laminar material may conveniently be substantially equal to the wall thickness of the tube or tubes. When the fins are formed from laminar material with both surfaces exposed to the fluid, the area of the surfaces of the fins that are exposed to the fluid per unit length of the tube is effectively directly proportional to the cross-sectional area of the flow path of the electric current that is provided by the fins. In these circumstances if it is arranged that, at the downstream one of the said two points, the temperature of the fins is substantially equal to the temperature of the wall of the tube, it will be found that the temperature of the fins decreases along the tube in the upstream direction, if they are so dimensioned, as to maintain the temperature of the wall of the tube substantially constant along its length. Although this variation in the temperature of the fins along the length of the tube can be avoided or reduced by increasing the thickness of the fins and at the same time decreasing their surface area to leave unchanged the cross-sectional area of the flow path of the electric current that they provide, the improved uniformity in the temperature of the fins does not result in any saving of metal.

The fins are advantageously integral with the tube. However, since this may give rise to constructional difficulties, the fins may be formed separately and secured to the interior of the tube by any suitable manner which provides electrical con-

tact between the fins and the wall of the tube, such as for example, welding or the like.

As noted hereinabove, the configuration of the fins can vary widely. Thus, the fins may be straight fins that extend, along their length, parallel to the axis of the tube, and their width, inwards (for example, radially inwards) from the wall of the tube. The width of the fins increases in the direction of flow of the fluid through the tube. Alternatively, each tube through which the fluid to be heated is passed may contain a tubular member that is coaxial with the tube and which is secured to the wall of the tube by planar fins. Such planar fins may extend, along their length, parallel to the axis of the tube and, across their width, radially, with the number of fins for a given distance along the length of the tube increasing in a stepwise manner in the direction of flow of the fluid through the tube. Instead of extending, along their length, parallel to the axis of the tube, the fins may be, for example, helical with the axis of the helix coinciding with the axis of the tube.

From the point of view of simplicity of construction, the wall thickness of the tube is advantageously uniform between the said two points. In this manner, the said variation in the total cross-sectional area of the flow path of the electric current results solely from a variation in the cross-sectional area, taken in a direction perpendicular to the axis of the tube, of the fins disposed within the tube. If desired, the thickness of the wall of the tube may be varied along the length of the tube. Thus, since the minimum thickness of the wall of the tube that will give the necessary strength is lower where the temperature of the wall is lower, the thickness of the wall may be decreased where the wall temperature is lower. It is in principle possible to thereby effect a saving of metal in the construction of the tube and fins. Furthermore, it is possible to effect a saving of metal, as compared with using a tube of uniform wall thickness and of which the temperature of the inner surface is maintained substantially uniform along the length of the tube between the said two points, by deliberately choosing the configuration of the fins so that the temperature of the inner surface of the wall of the tube is lower over a portion of the tube immediately downstream of the upstream of the said two points than elsewhere between the said two points, and decreasing the wall thickness of that portion of the tube correspondingly. The reason for this is that, where the temperature difference between the wall of the tube and the fluid is large, a small decrease in the temperature of the wall only slightly decreases the rate of transfer of heat from the wall to the fluid. However, at high temperatures, even a small decrease in the wall temperature considerably increases the mechanical strength of the material and significantly decreases the minimum wall thickness required.

The manner in which the said total cross-sectional area of the flow path of the electric current should vary along the length of the tube in order to obtain a given temperature distribution over the inner surface of the tube depends upon a number of factors including the mass velocity of the fluid through the tube, the initial temperature of the fluid, the maximum desired temperature of the surfaces exposed to the fluid and the like. It will also depend on the length of the intervals, if any, along the length of the tube between the points at which the fins are in electrical contact with the tube. Provided that the changes in the said total cross-sectional area remain small in each such interval, the effect of changes in the lengths of the intervals is small.

Although a substantially uniform temperature distribution requires that the said total cross-sectional area shall change continuously along the length of the tube, a satisfactory approximation of this can be achieved by arranging that the said total cross-sectional area changes in steps, with the cross-sectional area remaining substantially constant between successive steps. When this latter arrangement is adopted, if the fins are not in electrical contact with the tube in which they are situated continuously throughout their length, electrical contact between the fins and the associated tube may be conveniently provided in the region of each change in the said

total cross-sectional area. Furthermore, a substantially uniform temperature distribution necessitates the provision of fins of very small cross-sectional area towards the upstream one of the said two points. However, the constructional difficulties involved in providing such a very small cross-sectional area may outweigh the comparatively small advantage gained. An acceptable compromise is to continue the fins on for a certain distance in an upstream direction beyond the point where they reach the minimum convenient dimensions for a uniform temperature distribution along the wall of the tube. This may be accomplished by maintaining the cross-sectional area of the fins constant over the said certain distance at a value determined by the said minimum convenient dimensions and then terminating the fins entirely at a point downstream of the upstream one of the two points between which the electrical potential difference is applied.

The configuration of the tube or tubes and the method of supporting them must, of course take into account the thermal expansion and contraction that occurs in the tube during operation. Advantageously, there is provided a plurality of tubes arranged in pairs, the tubes of each pair (or the portions of the tubes that are provided internally with fins or other members) being straight and coaxial and the pairs of tubes (or the said portion of the tubes) extending parallel to one another. The inner or downstream ends of the tubes of each pair are connected to one or more outlet manifolds each of which is common to a plurality of pairs of tubes. The outer or upstream ends of the tubes are connected to supply manifolds through flexible couplings, such as for example, bellows or the like. This arrangement has the advantage of avoiding the need to provide flexible couplings where the tubes are at a very high temperature. When the fluid is a halide vapor and the surfaces of the tubes and fin that are exposed to the halide vapor are formed of platinum or an alloy thereof, the outlet manifold must of course also be constructed of platinum or an alloy thereof.

Because the fins are not in general at the same temperature as the wall of the tube, the configuration of the fins and the manner in which they are secured to the wall of the tube must in general take into account the possibility that differential expansion will occur between the wall fins the tube and the fins. In order to permit such differential expansion to occur without unduly high stresses being set up, the fins may be formed with small indents at intervals along their length. Although the small regions of reduced total cross-sectional area of the flow path of the electric current resulting from the presence of indents could result in local overheating, this can be reduced or eliminated by suitable design. Thus, if the regions of reduced cross-sectional area are sufficiently small, thermal conduction within the fins will suffice to prevent severe local overheating. Also, the temperature of the fins or other members can be reduced by increasing their surface area per unit mass and it will in general be appreciably below the desired maximum temperature except in the region of the downstream one of the said two points and therefore regions of increased temperature will not necessarily imply overheating. Furthermore, when the fins are in electrical contact with the tube in which they are situated only at intervals along the length of the tube, the magnitude of the electric current in the wall of the tube in any such interval is determined by the magnitude of the overall electrical resistance of the fins in the region and the effect of an indent in a fin on the overall resistance can be compensated for (at the expense of a small increase in the total quantity of platinum or platinum alloy required) by a small increase in the cross-sectional area of the fins or other members elsewhere in the interval.

When the fluid is a halide vapor as discussed hereinabove, the tubes are preferably constructed from a platinum-rhodium alloy containing within the range of from 5 percent to 25 percent by weight, preferably, within the range of from 10 percent to 15 percent by weight, of rhodium based on the weight of the alloy. If platinum-ruthenium or platinum-iridium alloys are used, the proportion of ruthenium or iridium, respectively,

is advantageously, within the range of from 5 percent to 25 percent (preferably 10 percent to 15 percent) by weight, based on the weight of the alloy. The fins may be constructed of the same material as the tubes. However, it may be preferred to construct the tubes of a platinum alloy and to construct the fins of platinum. This arrangement has the advantage that, if differential expansion occurs between the tube and the fins, the lower strength of the platinum will allow this to be taken up by deformation of the fins without setting up an undue stress in the tube, provided that the fins are of suitable configuration and are suitably secured to the wall of the tube.

If the electrical potential is applied to the tube through a member, for example, a manifold or another tube that has a surface exposed to the fluid, it may be necessary to insure that the said member does not reach too high a temperature. Advantageously, electrical connections are made to the tube only at the upstream of the said two points. Thus, when a plurality of tubes are arranged in pairs as explained hereinbefore, electrical connections are advantageously made to each tube only at the upstream end of the fins, or between that point and the flexible connection at the upstream end of each tube. Preferably, a positive DC potential is applied to one tube of each pair and a negative DC potential is applied to the other tube of each pair in this manner, with the common outlet manifold or conduit being grounded. If the cross-sectional area of the electrical flow path provided by the outlet manifold between the tubes of each pair is not sufficiently large to prevent overheating of the outlet manifold, the fins within the tubes may be continued through the manifold.

When an electrical connection is made to the tube to apply an electrical potential at the upstream one of the said two points, the tube is advantageously provided, immediately downstream of the electrical connection, with internal fins that are in electrical contact with the wall of the tube and that provide a flow path for the electric current of sufficient cross-sectional area to insure that the temperature of the wall of the tube in the immediate vicinity of the electrical connection is relatively low.

The electrical potential may be either DC or AC but, if it is AC the frequency must of course not be so high as to cause an appreciable "skin effect". This is due to the fact that the invention is based on the assumption that the current density is substantially uniform over the cross-sectional area of the flow path at any point along the tube except where materials of different resistivities are used together.

When there is provided a plurality of tubes arranged in parallel with respect to the flow of fluid between inlet and outlet manifolds, it is desirable to insure that the rate of flow of the fluid is substantially the same through each tube. If there are substantial pressure gradients within the manifolds, uniform distribution between the tubes requires either that the pressure drop across each tube shall be large by comparison with the pressure drops within the manifold or shall be compensated for by arranging that different tubes have different flow impedances, for example, by fitting the tubes with orifices of different sizes.

When the fluid is a halide vapor as aforesaid, the internal diameter of the tube may be within the range of from 0.5 to 2 inches. The optimum thickness of the wall of each tube depends to some extent on the internal diameter of the tube, but it is usually preferable for the wall thickness to be within the range of from 0.01 inch to 0.05 inch, preferably, about 0.02 inch.

An especially important application of the invention is to the preheating of titanium tetrachloride vapor, which may have in admixture with it aluminum chloride and/or silicon tetrachloride, prior to its vapor-phase oxidation in the manufacture of pigmentary titanium dioxide. When the halide vapor comprises titanium tetrachloride vapor, the temperature of the surfaces of the tube or tubes and of the fins that are exposed to the halide vapor preferably does not exceed 1,100° C. at any point. Above this temperature, the tubes and fins may tend to warp unless the apparatus is so constructed as to

insure that thermal stresses are kept at a very low level. Further, for the purpose of heating titanium tetrachloride prior to its vapor-phase oxidation to titanium dioxide, it is not usually necessary to heat the tube or tubes to a temperature exceeding 1,100° C.

The invention also provides a process and apparatus for the manufacture of titanium dioxide by the vapor-phase oxidation of titanium tetrachloride wherein the titanium tetrachloride is preheated by apparatus as hereinbefore described and comprising a tube or tubes provided internally with fins, the tube or tubes and the fins being constructed of platinum or an alloy thereof and being heated electrically. The invention further provides titanium dioxide whenever prepared by such a process.

The titanium tetrachloride vapor may be supplied to the tube or tubes at a temperature of about 160° C. the heated in the tube or tubes to a temperature of about 1,000° C. To pre-heat the titanium tetrachloride to a temperature of 1,000° C., the tubes will usually be heated to a temperature approaching 1,100° C.

The hot titanium tetrachloride vapors may then be used in the manufacture of titanium dioxide, such as for example, according to the process and apparatus disclosed in copending application Ser. No. 497,896, filed Oct. 19, 1965 now U.S. Pat. No. 3,512,219 issued May 19, 1970, to David R. Stern et al. for "PROCESS AND APPARATUS". Said patent discloses a process and apparatus for the manufacture of titanium dioxide by reacting titanium tetrachloride with an oxidizing gas in the vapor phase, which comprises means for separately pre-heating the titanium tetrachloride and the oxidizing gas, an elongated metal reaction chamber, a supply conduit for the oxidizing gas of which the downstream end is spaced from the upstream end of the reaction chamber to form a circumferentially extending inlet which serves as an inlet for the pre-heated titanium tetrachloride, a metallic annular distributing chamber surrounding and communicating with the inlet, at least a part of the inner surface of the distributing chamber being made of platinum or an alloy thereof. This arrangement of components is such that, in operation, the rate of flow of the titanium tetrachloride through the inlet is substantially constant along the length of the inlet and a jacket or jackets through which a coolant fluid can be passed in heat-exchanging relation with outer surface of only such part or parts, if any, of the said distributing chamber of which the inner surface is not made of platinum or an alloy thereof, but out of contact with the inner surface of the said portion.

One form of apparatus suitable for preheating titanium tetrachloride vapor prior to its vapor-phase oxidation in the manufacture of titanium dioxide and constructed in accordance with the invention will now be described by way of example with reference to the accompanying drawings.

Referring to FIGS. 1 and 2 of the accompanying drawings, the apparatus therein disclosed comprises 16 heating tubes, each indicated by the reference numeral 1, situated apart from their outer end portions, within an enclosure, indicated generally by the reference numeral 2, which is made of a non-metallic refractory material containing a high proportion of alumina and arranged to support the tubes 1 at intervals throughout their length. The enclosure may be heated, other than by radiation from the tubes, such as, for example, with heater means 22.

Within the enclosure 2, the tubes 1 are straight and the tubes of each pair are coaxial. The axes of the eight pairs of tubes are parallel to one another and lie in the same horizontal plane. At their inner, or downstream ends, the tubes 1 communicate with a horizontal transversely extending outlet conduit 3 which is closed at one end and which, at the other end, leads out of the enclosure 2. The downstream end portion 14 of each tube has an increased wall thickness to permit the transfer of electric current to the outlet conduit 3 without overheating. Further, the fins within the tubes may be continued through the conduit 3 as shown in FIG. 7.

Outside the enclosure 2, the outer, or upstream, end portions of the tubes 1 turn vertically downwards. At their outer ends, the tubes 1 are each formed (see FIG. 3) with an annular flange 4 which is secured to a similar flange 5 formed at the top of a flexible bellows 6. At the bottom of the bellows 6, there is formed an annular flange 7 which is secured to a similar flange 8 formed at the upper end of the branches of two inlet manifolds 9, one at each end of the heater.

The bellows 6 is made of an electrically insulating material and the top and bottom of each bellows are interconnected by an electrically insulating bar 10, which is pivotally mounted on the bellows at each end. Because each of the tubes 1 extends for only a short distance vertically as compared with its horizontal length, the relative movement between the outer end of the tube and the manifold 9, resulting from thermal expansion and contraction, is in a substantially horizontal direction and such movement is not prevented by the bar 10.

Just beyond the outer surface of the wall of the enclosure 2, the tubes 1 are formed with electrical connectors 11, which are arranged to be water-cooled.

Each tube is provided internally and within the enclosure 2 with an assembly of fins, which is indicated generally by the reference numeral 12. Each assembly 12 comprises eight fins 13 constructed in four pairs and welded at intervals along their length to short tubular spacers 14. Each pair of fins 13 is formed by bending a flat strip of laminar material, which is indicated generally by the reference numeral 15 (see FIG. 4) about its longitudinal center line so that the two fins 13 of each pair, that is to say, the portions of the strip 15 that lie on each side of its longitudinal centerline, are at an included angle of about 45°. The pairs of fins 13 are welded to the spacers 14 in the region of the said center line and are so orientated that the included angle between adjacent fins of different pairs are also at an included angle of about 45° (see FIG. 6).

Referring to FIG. 4, it will be seen that the width of each strip 15 is at a constant maximum value over short lengths 16 of the strip and over a rather longer length 17 at one end of the strip. The width of the portions 18 of the strip that lie between the wide portions 16 and 17 increase from one portion 18 to the next along the strip towards the portion 17. Referring to FIG. 5, it can be seen that the wide portions 16 are very short (in the direction of the length of the fins 13) as compared with the length of the graduated portions 18. Similarly, the spacers 14 are very short by comparison with the separation between them.

The fin assemblies 12 are inserted into the tubes 1 with the wide portions 17 of the strips 15 at the downstream ends of the tubes 1 and the outer extremities of the wide portions 16 and 17 are each welded to the walls of the tubes 1. Thus, each fin assembly 12 is secured in the associated tube 1 in such manner that the spacers 14 are coaxial with the tube, and the fins 13 are each in electrical contact with the wall of the tube 1 at each point where they are welded to the tube.

The fin assemblies 12 terminate, at their upstream ends, downstream of the inner surface of the wall of the enclosure 2, but each tube 1 is provided internally, immediately on the downstream side of the connector 11, with a second fin assembly 21. Each fin assembly 21 resembles the fin assemblies 12 in being made of eight radially extended fins formed in pairs by bending four strips about their longitudinal center lines, the fins being welded to a cylindrical spacer 14 and (at its ends wherein the fins are widest) to the wall of the tube. The fin assemblies 21 are, however much shorter than the fin assemblies 12 and, except for their wider end portions, the fins of the assemblies 21 are of uniform width along their length.

Again referring to FIG. 4, each strip 15 is provided with small holes 19 along its center line to facilitate bending the strip to form the fins 13 and with indents 20 arranged to allow differential expansion to take place between the fins 13 and the wall of the tube 1 without unduly large stress being set up. As explained hereinbefore, such small indents 20 do not, with correct design, lead to overheating, and the same considerations apply to the holes 19.

As an example of suitable dimensions, the thickness of the walls of the tubes 1 and of the laminar material of which the fins are constructed may be 0.020 inch. The diameter of the holes 19 may be one-sixteenth inch. The internal diameter of the tubes 1 may be 1 inch and the length of each tube may be about 12 to 15 feet. The length of the graduated portions 18 of the strips 15 may vary, in a given strip, from about 2 feet at the upstream end to about 9 inches at the downstream end, assuming that there are six such portions. The length of each of the wide portions 17 of the strips 15 may be 0.25 inches. The internal diameter of the outlet conduit 3 may be 3 inches and the thickness of its wall may be 0.030 inches.

While the tubes 1 and the outlet conduit 3 are preferably constructed from a platinum-rhodium alloy containing 10 percent by weight of rhodium, the fin assemblies 12 and 21 are preferably constructed from platinum in order to facilitate deformation of the fin assemblies to take up differential thermal expansion of the assemblies and the wall of the tube 1 (as is explained hereinbefore).

In operation, the outlet conduit 3 and the supply manifold 9 are electrically earthed. A positive DC potential is applied to the connectors 11 at one end of the enclosure 2 and a negative DC potential is applied to the connectors 11 at the other end of the enclosure 2, the absolute magnitudes of these potentials being the same. Thus, for each pair of tubes 1, an electric current is caused to flow from the connector 11 on one tube of the pair, through that tube and the two fin assemblies 21 and 12 in that tube, through the wall of the outlet conduit 3, and then through the other tube 1 of the pair and the two fin assemblies 12 and 21 in that tube to the connector 11 on that tube.

Considering a single tube 1 and neglecting the effect of the spacers 14, the wide portions 16 of the strips 15 from which the fins are formed, the holes 19 and the indents 20, the total cross-sectional area of the flow path of the electric current is large immediately downstream of the connector 11 on the tube owing to the presence of the fin assembly 21. At the downstream end of the fin assembly 21, the cross-sectional area decrease suddenly to its minimum value, which is the cross-sectional area of the tube wall alone, and then increases in a stepwise manner owing to the presence of the fin assembly 12. Finally, the cross-sectional area of the flow path of the electric current provided by the outlet conduit 3 is somewhat greater than the cross-sectional area provided by the wall of the tube 1 and the fin assembly 12 at its downstream end. Thus, the electrical resistance per unit length of the tube is low immediately downstream of the connector 11 owing to the presence of the fin assembly 21, but, at the downstream end of that assembly, it rises suddenly to a maximum value and then decreases in the downstream direction in a stepwise manner. Therefore, the tube wall may be of decreased thickness 1b immediately downstream of connector 11.

Because the magnitude of the electric current is constant along the length of each tube 1, the rate of generation of heat per unit length of the tube is directly proportional to the resistance per unit length. Thus, the rate of generation of heat is relatively low immediately downstream of the connector 11, which (together with the water cooling of this connector) prevents the connector 11 from reaching too high a temperature. Immediately downstream of the fin assembly 21, the rate of generation of heat per unit length of the tube 1 rises sharply and thereafter falls in a stepwise manner in the downstream direction.

The titanium tetrachloride vapor, which may have minor quantities of other chlorides in admixture with it, is admitted through the supply manifold 9 and its temperature rises progressively as it passes along the tubes 1 to the outlet conduit 3.

The temperature of the wall of each tube 1 rises in the downstream direction over each section of the tube for which the total cross-sectional area of the flow path of the electric current is constant and rises more sharply at the downstream end of the fin assembly 21 where the said total cross-sectional area decreases. Where, as a result of the configuration of the

fin assemblies 12, the said total cross-sectional area increases in a downstream direction, the temperature of the walls of the tubes 1 drops. Thus, the temperature profile of the wall of each tube 1 along its length is of roughly sawtooth form over the length occupied by the fin assembly 12 and it falls away in an upstream direction beyond the upstream end of this assembly. The changes in the said total cross-sectional area are so chosen and situated in relation to the mass velocity of the vapor and the degree of external cooling of the tubes 1 (which is described hereinafter) that the peaks of the temperature profile are each at a temperature just below the maximum that can be tolerated.

The temperature of each fin assembly 12 tends to decrease in the upstream direction, but (as is explained hereinbefore) this is not of any particular significance.

The inner surfaces of the walls of the enclosure 2 are maintained at a temperature below that of the tubes 1, which (as is explained hereinbefore) makes it possible to reduce the weight of platinum or platinum alloy in the fin assemblies 12 that is necessary in order to prevent overheating of the walls of the tubes 1.

What is claimed is:

1. A process for heating a fluid which comprises passing the fluid through a metal tube that is provided internally with metal fins arranged to increase the area of contact with the fluid and being in electrical contact with the wall of the tube, and heating the wall of the tube and the fins by applying an electrical potential difference between two points spaced apart along the length of the tube to thereby cause an electric current to flow through both the wall of the tube and the fins, establishing the configuration such that the total cross-sectional area of the tube wall and fins in the flow path of the electric current between the said two points increases, at least over a length of the tube immediately upstream of the downstream one of the said two points, in the direction of flow of the fluid in such manner as to tend to prevent the temperature of the inner surface of the wall of the tube that is exposed to the fluid from increasing in the direction of flow of the fluid, and establishing the configuration of said fins such that the temperature of the fin surfaces that are exposed to the fluid nowhere substantially exceeds the maximum temperature of the inner surface of the wall of the tube between the said two points.

2. A process as defined in claim 1, wherein the temperature is controlled to insure that the inner surface of the tube and of the surfaces of the fins that are exposed to the fluid nowhere exceeds 1,100° C.

3. A process as defined in claim 1, wherein the tube is situated in a thermally insulated enclosure and heat is supplied to the boundaries of the enclosure other than by radiation from the tube.

4. A process as defined in claim 1, wherein the tube is situated in a thermally insulated enclosure having walls that are maintained at a temperature below the temperature of the outer surface of the tube at the downstream one of the said two points.

5. A process as defined in claim 1, wherein the flow rate of the fluid through the tube, the magnitude of the electric potential applied between the said two points and the configuration of the fins are such that, over at least 50 percent of its area between the said two points, the temperature of the inner surface of the tube that is exposed to the fluid is within 200° C. of the highest temperature at any point of the said inner surface that is exposed to the fluid.

6. A process as defined in claim 5, wherein the flow rate of the fluid through the tube, the magnitude of the electric potential applied between the said two points and the configuration of the fins are such that over at least 80 percent of its area between the said two points, the temperature of the inner surface of the tube that is exposed to the fluid is within 50° C. of the highest temperature at any point of the said inner surface that is exposed to the fluid.

7. A process as defined in claim 1, wherein the flow rate of the fluid through the tube, the magnitude of the electric potential applied between the said two points and the configuration of the fins are such that the temperature of the inner surface of the tube that is exposed to the fluid is, everywhere between the said two points except in the immediate vicinity of the upstream point, within a range of 300° C.

8. A process as defined in claim 7, wherein the flow rate of the fluid through the tube, the magnitude of the electric potential applied between the said two points and the configuration of the fins are such that the temperature of the inner surface of the tube that is exposed to the fluid is, everywhere between the said two points except in the immediate vicinity of the upstream point within a range of 150° C.

9. A process as defined in claim 8, wherein the cross-sectional area of the wall of the tube is substantially uniform between the said two points and the flow rate of the fluid through the tube, the magnitude of the electric potential applied between the said two points and the configuration of the fins are such that the temperature distribution over the inner surface of the tube that is exposed to the fluid is substantially uniform between the said two points except in the immediate vicinity of the upstream point.

10. A process as defined in claim 1, wherein the said electrical potential difference is a DC potential difference.

11. Apparatus for heating a fluid which comprises a metal tube through which said fluid can be passed, metal fins provided internally of said tube, said fins being arranged to increase the area of contact with said fluid and being in electrical contact with the wall of said tube, and means for applying an electrical potential difference between two points spaced apart along the length of the tube to cause an electrical current to flow through the wall of said tube and said fins and thereby heat said tube and said fins, the configuration of said fins being such that the total cross-sectional area of said tube wall and said fins increases along the tube in one direction in such a manner that when said fluid is caused to flow through the tube in the direction in which said cross-sectional area increases and the tube and fins are heated by applying an electrical potential difference between said two points, the said increase in cross-sectional area tends to prevent the temperature of the inner surface of the wall of the tube that is exposed to the fluid from increasing in the direction of flow of the fluid, at least over a length of the tube immediately upstream of the downstream one of the said two points, and the temperature of the surfaces of the fins that are exposed to the fluid nowhere substantially exceeds the maximum temperature of the inner surface of the tube between the said two points.

12. Apparatus as defined in claim 11, wherein said fins are formed from laminar material with both surfaces of the laminar material exposed to the fluid.

13. apparatus as defined in claim 11, wherein said fins are straight fins that extend, along their length, parallel to the axis of the tube in which they are situated and, across their width, inwards from the wall of the tube, the width of the fins increasing in one direction along the tube.

14. Apparatus as defined in claim 13, wherein the fins extend, across their width, radially inwards from the wall of the tube in which they are situated.

15. Apparatus as defined in claim 11, wherein the wall thickness of said tube is substantially uniform between the said two points.

16. apparatus as defined in claim 11, wherein the configuration of said fins is such that, in operation, the temperature of the inner surface of the wall of the tube is lower over a portion of the tube immediately downstream of the upstream one of the said two points than elsewhere between the said two points and the said portion of the tube is of decreased wall thickness.

17. Apparatus as defined in claim 11, wherein the total cross-sectional area of said tube wall and said fins increases in a stepwise manner in the said one direction.

18. Apparatus as defined in claim 17, wherein said fins are in electrical contact with the tube in which they are situated in the region of each change in the said total cross-sectional area.

19. Apparatus as defined in claim 11 which comprises a plurality of said metal tubes, each provided internally with said fins and so interconnected as to enable fluid to be caused to flow through them in parallel.

20. apparatus as defined in claim 19, which also comprises a thermally insulated vessel within which each metal tube is situated.

21. Apparatus as defined in claim 20, wherein there is provided means for heating the wall of said vessel other than by radiation from the defined tubes.

22. Apparatus as defined in claim 11, which comprises a plurality of said metal tubes each provided internally with said fins, said tubes being arranged end to end in pairs, the tubes of each pair, at least over the lengths thereof wherein the fins are situated, being straight and coaxial and the pairs of tubes extending, at least over the said lengths, parallel to one another, the inner ends of the tubes of each pair being connected to at least one outlet manifold common to a plurality of pairs of tubes and the outer ends of the tubes being connected to supply manifolds through flexible couplings.

23. Apparatus as defined in claim 22, wherein the said flexible couplings are bellows.

24. Apparatus as defined in claim 22, wherein, in order to enable the said electrical potential difference to be applied between the said two points, an electrical connection to each tube is made only at what, in operation, is the upstream one of the said two points and the inner ends of said pairs are electrically connected.

25. Apparatus as claimed in claim 24, wherein the electrical connection to each tube is at a point at what, in operation, is the upstream end of the fins.

26. Apparatus as defined in claim 22, wherein said fins situated within the tubes of each of the said pairs of tubes are continued through said outlet manifolds.

27. Apparatus as defined in claim 24, wherein each tube is provided, immediately downstream of the said electrical connection, with additional internal fins that are in electrical contact with the wall of the tube and that provide a flow path for the electric current of sufficient cross-sectional area to ensure that the temperature of the wall of the tube in the immediate vicinity of the electrical connection is, in operation, relatively low.

28. Apparatus as defined in claim 11, wherein said fins are formed, at intervals along their length, with small indents so arranged as to reduce thermal stresses resulting from differential expansion between the wall of the tube and the fins.

29. Apparatus as defined in claim 11, wherein the tube is formed of an alloy selected from the group consisting of a platinum-rhodium alloy, a platinum-ruthenium alloy and a platinum-iridium alloy.