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Sloan

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[54] **ZONE-MELTING APPARATUS**

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[52] **U.S. Cl.** ..... **23/273 SP,** 23/301 SP

[51] **Int. Cl.** **B01j 17/03**

[58] **Field of Search** ..... 23/273 SP, 273 F, 301 SP

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[57] **ABSTRACT**

Disclosed herein is a zone-melting apparatus for zone-melting especially suitable for the purification of organic compounds. Apparatus improvements include provision of thermally conducting members within the container that extend radially into and contact the sample, and/or cooling elements designed to contact the container externally without inhibiting rotatability thereof. The process improvements include stirring the liquid zone within the container and/or cooling the sample by contacting the outside of the container with a porous cooling element.

4 Claims, 3 Drawing Figures

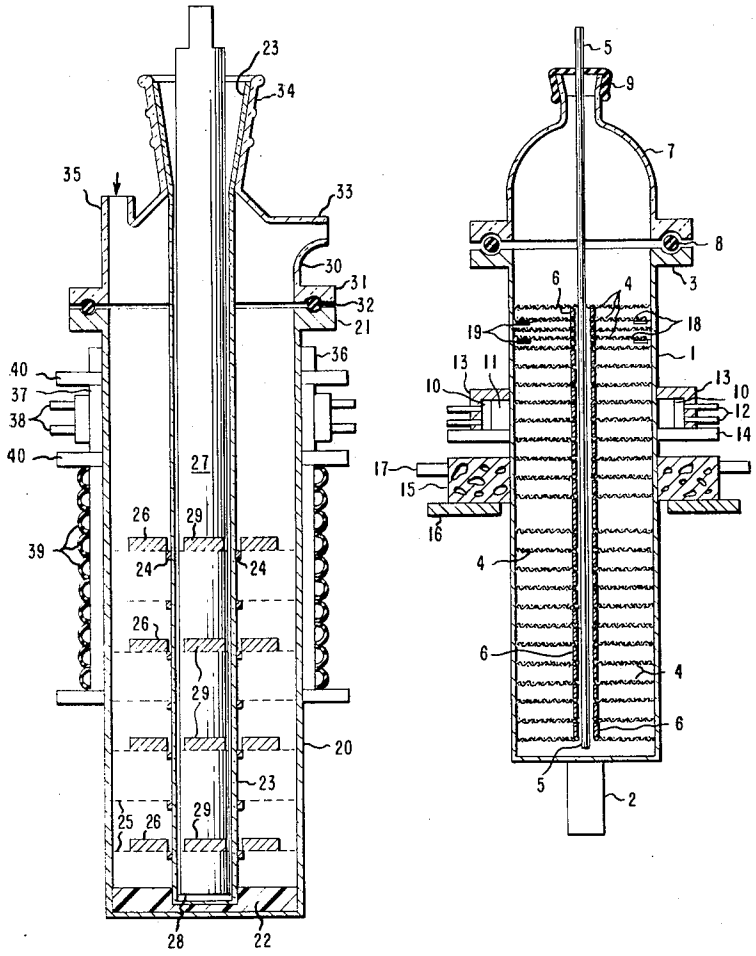


FIG. 2

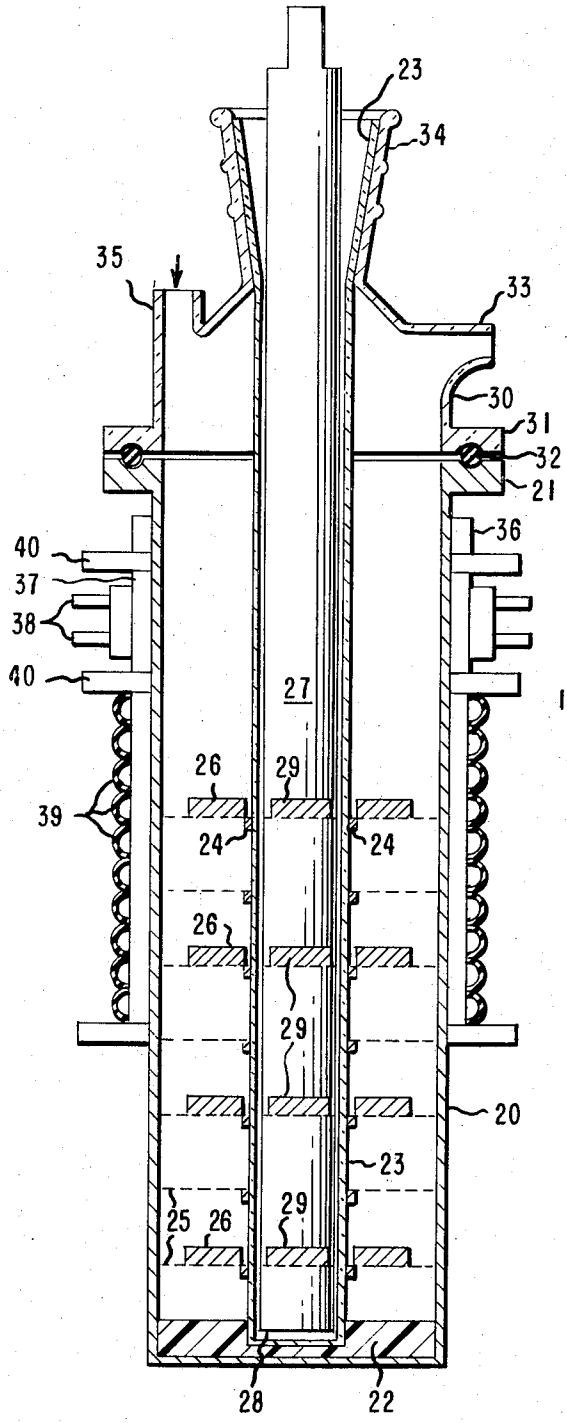
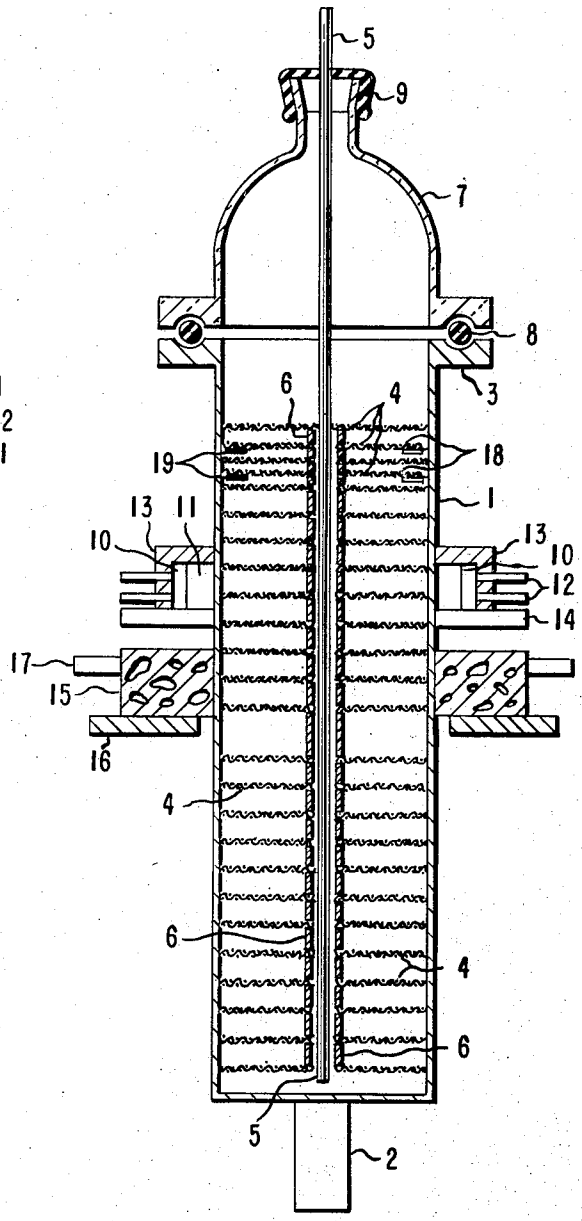


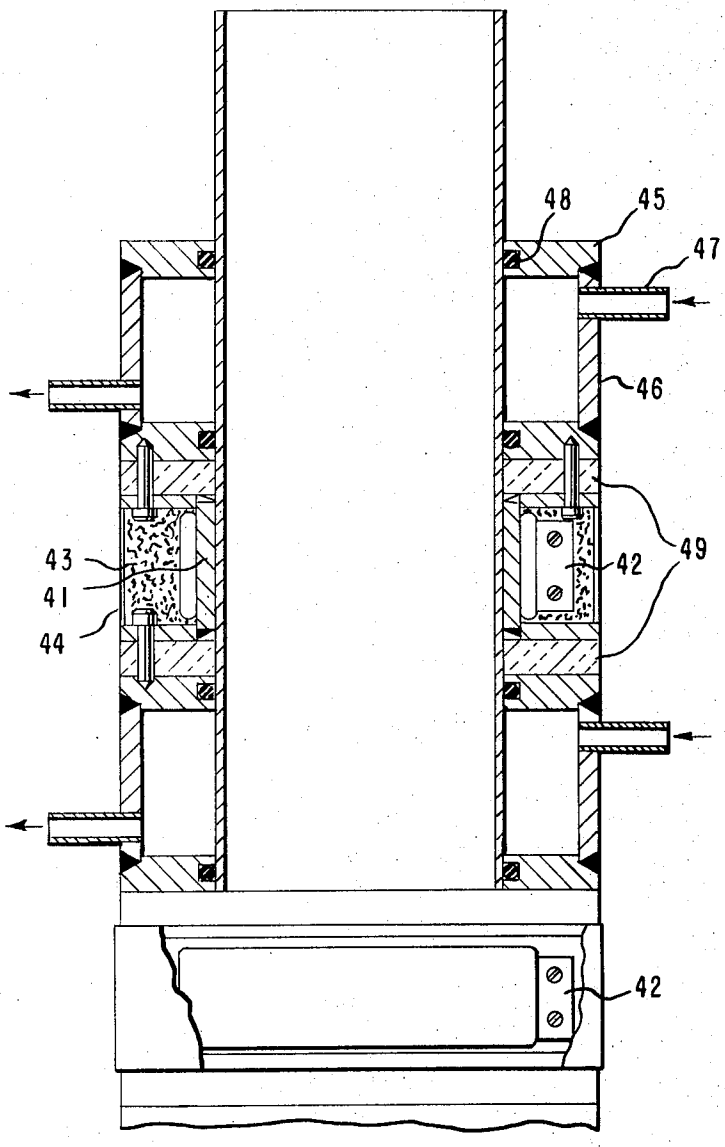
FIG. 1



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FIG. 3



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ZONE-MELTING APPARATUS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to zone-melting and more specifically to a process and apparatus therefor.

2. Description of the Prior Art

Zone-melting makes use of the principle that when a homogeneous liquid mixture is cooled, the composition of the solid that crystallizes out from the liquid is usually different from the composition of the liquid. Short zone lengths can be most desirable in zone-melting and refining. A typical zone-melting process is a multipass operation and it is often advantageous to provide many molten zones and cooling zones within a given length of material to minimize the size of the apparatus and the processing time.

Attempts to achieve short zone lengths are exemplified by U.S. Pat. No. 3,423,189 wherein the zone length is reduced by disposing the cylindrical charge tube horizontally and slowly rotating the tube about its own axis as well as by employing a coolant to cool the (solid) regions between the molten zones. The coolant is confined by its own surface tension between the tube and the annular rings surrounding it with the attendant difficulty of maintaining the coolant in contact with the tube.

Another problem in the purification or organic compounds by zone-melting is their low thermal conductivity (Herington, "Zone Melting of Organic Compounds," John Wiley and Sons, New York, 1967). This property alone dictates the use of very low zoning speeds. The direct application of coolant to a sample tube as taught in U.S. Pat. No. 3,423,189, effects rapid solidification of the molten material adjacent to the container wall, but further solidification is impeded by the low thermal conductivity of the sample.

SUMMARY OF THE INVENTION

Apparatus

It is characteristic of the invention taught herein that in a zone-melting apparatus that includes

a sample-holding container,

heating and cooling elements alternately adjacent one another and designed to surround the container and the sample therewithin, and

means for providing relative motion between the container and said heating and cooling elements,

the novel improvement comprises one of the group consisting of

a. thermally conducting members radially disposed within the container, designed to extend into and contact the sample to
   i. promote even heat transfer therethrough and
   ii. stir the sample during rotation of the container (when weights or magnets are attached near the periphery of said members),
b. porous cooling elements designed to contact the container without inhibiting its rotatability, and
c. a combination thereof.

The apparatus consists essentially of:

1. an elongated axially rotatable sample-container made from a chemically inert material such as glass, metal or ceramic, having incorporated therein

2. thermally conducting elements or discs which facilitate heat transfer through the container radially but not axially, said elements attached to an aligning tube disposed lengthwise in the container in such a way that they are at least partially rotatable about said aligning tube, said elements adaptable (e.g., with weights or magnets attached) to act as stirrers for the contents of the container; said elements can be fabricated from any material of high thermal conductivity which is chemically compatible with the sample to be purified such as aluminum or copper for inert, neutral compounds, stainless steel for more reactive ones and noble metals for highly corrosive ones, and a
3. heater/cooler assembly containing heating and cooling members alternately disposed, said assembly designed to surround the container as will be discussed more fully hereafter, said cooler being characterized in that the cooling members are porous and are in contact with the container.

The apparatus disclosed herein features one or both of porous cooling elements for holding cooling liquid in contact with the sample container regardless of the surface tension of the liquid, and thermal conductivity members within the tubes extending into the sample radially to aid in heat transfer, to eliminate super-heating near the container wall, and to make it possible to operate with lower heater temperatures. The thermal conductivity members are also adaptable to be used to stir the sample in the container. Large sample sizes of the order of kilograms can be processed and purified in larger containers than could heretofore be used. For instance, containers in excess of two inches in diameter can be employed herein. The apparatus can be employed for organic and inorganic chemicals melting between about −60°C. and 350°C.

Generally, the heater/cooler battery is horizontally or nearly horizontally disposed, and the sample container tube is moved through it at velocities of about 1 to 25 mm per hour. In order to avoid radial dissymmetry of the molten zones, the tube is rotated as it traverses the heater/cooler battery, at about 1 to 5 revolutions per minute. Alternatively, the heater/cooler battery can be revolved around the sample-container tube.

In one embodiment of this invention, small weights are affixed to the periphery of the heat-conducting elements, e.g., discs, so that they cease to rotate fully with the external tube, but swing in a small arc to act as oscillating stirrers. It is not necessary that all of the heat-conducting elements have weights attached thereto. It may be desirable that only some of the discs bear said weights and be symmetrically or unsymmetrically arranged in relation to the unweighted discs and/or the heater/cooler assembly. It is also contemplated that the heat conducting elements, with or without attached weights, can be of varying thickness and/or diameter within the same zone-melting system.

In another embodiment of this invention, an annular charge is contained between two concentric, vertical tubes. Bar magnets are mounted in a shaft disposed lengthwise within the inner tube, said shaft being rotatable within the inner tube. Said inner tube may also be considered an aligning tube for the discs. Perforated stainless-steel or aluminum discs are supported on the outer surface of the inner tube and are disposed radially therefrom toward the inside of the outer tube or container. Each perforated disc can be adapted to bear

two bar magnets whose north and south poles are placed in juxtaposition to the south and north poles, respectively, of one of the magnets in the shaft. Thus, each magnet bearing heat transfer disc becomes a magnetically driven stirrer which is free to rotate when it is within a liquid zone and when the shaft is rotated. Within the framework of this disclosure, it will be understood by those skilled in the art that the size and spacings of the disc perforations as well as the thickness of the discs, etc., can be optimized to meet particular goals. For instance, smaller and fewer perforations favor heat conductivity over radial fluid flow. It should also be recognized that the stirrers employed herein are adapted to rotate only in the liquid zone and the magnets are not so powerful as to drive them through the solid zone of the sample.

Mechanical stirring offers advantages separate from those conferred by the presence of thermally conducting members; it decreases the thickness of the liquid layer at the solid-liquid interface wherein transport is diffusion controlled. This results in improved segregation of impurities through the avoidance of constitutional supercooling.

The use of porous liquid applicators simplifies the direct application of liquid coolant to moving sample tubes. In the art, where direct application is effected via open annuli, in which coolant is retained by its own surface tension, precise machining and assembly of the cooler elements is required. Moreover, it requires the use of sample containers which are of very uniform diameter, precise circularity of cross section, and high straightness. None of these too-rigid criteria is critical when the novel porous liquid applicators are used.

Process

A general zone-melting process comprises placing the material (sample) into a tube-container therefor and alternately melting (by heaters) and cooling (by coolers) portions of the material and providing alternate zones of melted and cooled (solid) material, said zones alternately disposed circumferentially about the tube, and moving the molten zones along the axis of the tube by rotating and translating said tube about its axis relative to the heater(s)/cooler(s).

It is characteristic of the invention taught herein that in a zone-melting process that includes

forming at least one molten zone in a sample of material in a container surrounded by at least one heating and cooling element, and

passing the molten zone along the axis of the container,

the novel improvement comprises one of the group consisting of

a. stirring the sample and improving heat transfer therethrough, by means of thermally conducting elements disposed radially within the container,

b. cooling the sample by contacting the outside of the container with a porous cooling element, and

c. a combination thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The various aspects of the invention will become more apparent upon consideration of the following drawings which are meant to illustrate the novel apparatus of this invention. It should be noted in connection with the drawings that there are spaces (too small to be depicted therein) between the discs and the inside container wall and between the heater-cooler assembly and the outside container wall.

FIG. 1 Cross sectional view of a one liter capacity zone melting apparatus of this invention.

FIG. 2 Cross sectional view of the radial heat conducting elements for the apparatus of FIG. 1.

FIG. 3 Cross sectional view of an alternate heater/cooler assembly system of the apparatus of FIG. 2.

DETAILS OF THE INVENTION AND DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. 1 the sample container consists of a stainless steel tube **1**, 28 in. long, with inside diameter and outside diameter of 1.875 in. and 2.000 in. respectively. A stainless steel shaft **2** is welded to the closed end of the tube, to provide a connection for transporting and rotating the tube. A grooved, stainless steel flange **3** is welded to the open end of the tube, to provide secure closure.

An assembly of heat conductors is constructed by sliding discs **4** of 20-mesh stainless steel screen, of 0.125 in. inside diameter and 1.825 in. outside diameter onto stainless steel aligning tube **5**, which is 36 in. long and of inside diameter 0.078 in. and outside diameter 0.125 in., with its inner end closed. Discs **4** are separated from one another by Pyrex glass spacers **6**, 0.25 in. long of 0.158 in. inside diameter and 0.236 in. outside diameter.

The sample container is closed by means of Pyrex glass cap **7** and O-ring **8**. Aligning tube **5** emerges from cap **7** through a rubber seal **9**. A thermocouple (not shown) is inserted into tube **5** in order to measure the temperatures at various points in the tube; in this way, settings of heaters and coolers may be corrected until a sequence of alternating zones of liquid and solid result.

Cylindrical band heaters **10** are clamped onto aluminum heater cores **11**, 0.750 in. long and of inside diameter 2.010 in. and outside diameter 2.500 in. An adjustable voltage is applied to terminals **12**. Asbestos insulation **13** is applied to the exposed heater and heat-core surfaces. Heater cores **11** are affixed to Transite mounting plates **14**, which are in turn, attached to a rigid, metal support (not shown).

Cellulose sponges **15**, approximately 3 in. by 4 in. and with central bores of 1.75 in. diameter are cemented to aluminum plates **16**. Tubes **17** deliver water or other coolant liquid to sponges **15**, at a rate controlled by a separate valve for each tube.

One or more heat-conducting, stirrer discs of 20-mesh stainless steel screen **18** can be placed between pairs of discs **4**, separated from one another by Pyrex glass spacers **6**. Discs **18** are of 0.125 in. inside diameter and 1.75 in. outside diameter. Attached near the periphery of discs **18** are weights **19**, consisting of discs of lead weighing about 5 gm. When the assembly of discs is inserted into the sample container tube and the latter is rotated at speeds of, say, 40 revolutions per minute or higher, the unsymmetrically weighted discs oscillate through an arc of about 45° to either side of their equilibrium positions. This oscillation produces a vigorous stirring action within each molten zone.

In tubular sample containers of diameter greater than 1.0 to 1.5 inches, many compounds solidify so slowly that the rate of zoning must be extremely slow, such as about 1 mm. per hour, in order to maintain discrete

zones. The insertion of thermally conductive elements overcomes this problem. Thus, with thermal conductors in the sample tube, zone melting can be applied to materials with low intrinsic rates of solidification, such as waxes and fatty materials.

In FIG. **2** the sample container of the zone melter is a tube **20** fabricated of type-316 stainless steel; the tube has 3.875 in. inside diameter and has an outer surface that has been centerless ground to 3.997 in. outside diameter, with an RMS-16 finish. An RMS-16 finish indicates that the root-mean square of the surface irregularity is 16 micro-inches. This has been found to be optimum for smooth passage of the O-rings over the surface. The container **20** is 48 in. long, and bears at its upper end a stainless steel flange **21.** A sample container of Pyrex glass, 100 mm. outside diameter and 95.4 mm. inside diameter, has also been used. An annulus **22** of Teflon polytetrafluoroethylene resin centers the bottom of Pyrex tube **23** in container **20.** Aluminum rings **24** are affixed to tube **23** at 1-inch intervals by means of a heat-resisting silicone cement; rings **24** are ⅛ in. thick, and have inside diameter and outside diameter of 1.275 in. and 1.500 in. respectively.

Resting on rings **24** are discs **25,** of perforated aluminum; these are 0.030 in. thick and have inside diameter and outside diameter of 1.275 in. and 3.250 in. respectively. The perforations in discs **25** are of 0.15 in. diameter, and are spaced at a center-to-center distance of 0.175 in. Bar magnets **26** are affixed to discs **25** by means of heat-resisting silicone cement. Magnets **26** are **1** in. long and 5/16 in. in diameter. A nylon shaft **27** is centered within tube **23** by means of O-ring **28.**

In operation, shaft **27** is rotated at about **50** revolutions per minute by an electric motor (not shown). Magnets **29** are pressed into holes bored through **27** at **2** in. intervals; these have the same dimensions as magnets **26.** It should be noted that magnets **26** are attached to discs **25** in such a manner that both magnets on a given disc are attracted to the associated magnet **29.**

The sample container **20** is closd by means of a Pyrex cover **30,** bearing a grooved flange **31** in which O-ring **32** is situated. Cover **30** is also equipped with a tubular port **33,** to which a vacuum pump and/or gas inlet may be attached, a standard-taper joint **34** to which a mating joint of tube **23** is sealed, and a tubular port **35** through which container **20** may be filled.

An assembly of heaters and coolers is shown consisting of an aluminum pipe **36, 36** in. long, of inside diameter and outside diameter 4.026 in. and 4.500 in. respectively. Pipe **36** is provided with ten pairs of slots, covered by asbestos based, high temperature insulation, **40,** 0.500 in. wide at alternating spacings of 2.50 in. and 3.00 in. The pipe is thus segmented into annuli of 2.00 in. and 2.50 in. heights, joined by the narrow columns of metal remaining between each pair of slots. The narrower segments, five in number, are fitted with electrical resistance heaters **37,** to which an adjustable voltage is applied via terminals **38.** The wider segments are wrapped with rubber tubing **39** of high thermal conductivity, with semicircular cross section. The heated and cooled segments of the pipe **36** are insulated from one another by semiannuli of asbestos-based, high temperature insulation, **40,** ½ in. thick, which fill the slots between the heated and cooled segments.

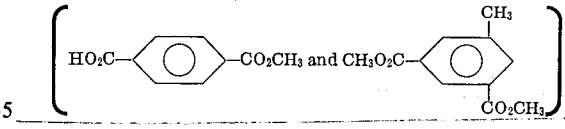
FIG. **3** shows an alternative heater/cooler assembly. Aluminum heater bodies **41,** 2.00 in. tall, with inside diameter of 4.026 in. and 4.500 in. respectively, are fitted with clamped-on electrical resistance heaters **42.** Glass fiber insulation **43** is wrapped around heaters **42** to fill the space defined by the flanges of the heater body, and the entire assembly is enclosed in a cover consisting of a band of 20-gauge aluminum **44.**

Aluminum cooler-bodies are made from pairs of aluminum annuli **45,** 0.50 in. thick, and of inside diameter and outside diameter 4.000 in. and 6.620 in. respectively, welded to segments of aluminum pipe **46,** 2.375 in. high and of inside diameter and outside diameter 6.065 in. and 6.620 in. respectively. Segments **46** are equipped with inlet and outlet tubes **47,** through which liquid or gaseous coolant enters and leaves. The cooler-bodies are sealed to the surface of the sample container by means of O-rings **48** emplaced in grooves within annuli **45.** The cooler-bodies are separated from the heater-bodies by annular Marinite insulators **49.**

Either of the heater/cooler assemblies can be transported along the sample container at speeds between about 0.1 in. per hour and 1 in. per hour; or, the sample container can be moved within the heater/cooler assemblies at such speeds.

EXAMPLE

A charge of **6.5** kg. of dimethyl terephthalate (m.p. 140°C.) containing an impurity therein



was transferred from a heated reservoir into the sample container of FIG. **2** under nitrogen pressure. Heating and cooling were adjusted after visual inspection, until discrete molten and solid zones were present. The heater/cooler assembly was moved along the sample container at 1.5 cm. per hour. After **2** hours the sample container fractured. The contents were cooled and removed from the container. The impurity was found to be segregated in each of the molten zone areas and the dimethyl terephthalate in each of the solid zone areas.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a zone melting apparatus that includes a cylindrical sample-holding container,

heating and cooling elements alternately adjacent one another surrounding the container, and

means for providing longitudinal relative motion between the container and said heating and cooling elements, whereby at least one molten zone is formed in a normally solid sample container in said container and moves longitudinally in said container with said heating and cooling elements, the improvement which comprises:

a plurality of thermally conducting members radially disposed within the container, spaced at fixed positions along the length thereof and extending into the sample, at least some of said members being independently rotatable stirrer members while in the molten zone of the sample,

and means to rotate said rotatable stirrer members while in said molten zone said sample holding container being substantially horizontal and said thermally conductive members being perforate discs spaced alone an axial aligning tube, in said container at least some of said discs being stirrer members having weights attached unsymmetrically thereto whereby said stirrer members oscillate in an arc while in a molten zone on rotation of said container.

2. Apparatus of claim **1** wherein said discs are of wire mesh.

3. Apparatus of claim **2** wherein alternate discs are stirrer discs.

4. In a zone melting apparatus that includes a cylindrical sample-holding container,

heating and cooling elements alternately adjacent one another surrounding the container, and means for providing longitudinal relative motion between the container and said heating and cooling elements, whereby at least one molten zone is formed in a normally solid sample container in said container and moves longitudinally in said container with said heating and cooling elements, the improvement which comprises:

a plurality of thermally conducting members radially disposed within the container, spaced at fixed positions along the length thereof and extending into the sample, at least some of said members being independently rotatable stirrer members while in the molten zone of the sample,

and means to rotate said rotatable stirrer members while in said molten zone, said thermally conductive members being perforate discs spaced along an axial aligning tube in said container and at least some of said discs having magnets attached thereto,

a shaft disposed lengthwise in said axial aligning tube, and means to rotate the said shaft, said shaft having magnets mounted thereon in juxtaposition to the magnets on said discs whereby on rotation of said shaft the discs bearing magnets rotate while in a molten zone.

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