(12) UK Patent Application (19) GB (11) 2 119 385 A

(21) Application No 8311499
(22) Date of filing 27 Apr 1983
(30) Priority data
(31) 374015
(32) 3 May 1982
(33) United States of America (US)
(43) Application published 16 Nov 1983
(51) INT CL[3] C08F 8/50 114/26
(52) Domestic classification C3J AE AK C3W 222 H5R 10 12 U1S 1452 1555 1627 C3J H5R
(56) Documents cited EP 0017349 GB 1516648 GB 1505284 GB 1019440
(58) Field of search C3J C3L H5R

(71) Applicant
Shamrock Chemicals Corporation (USA—New Jersey), Foot of Pacific Street, Newark, New Jersey 07114, United States of America
(72) Inventors
William B. Neuberg, Robert Luniewski
(74) Agent and/or Address for Service
Kilburn and Strode, 30 John Street, London WC1N 2DD

(54) Apparatus and method for radiation processing of materials

(57) A method and apparatus for radiation degradation processing of polytetrafluoroethylene makes use of a simultaneous irradiation, agitation and cooling. The apparatus is designed to make efficient use of radiation in the processing.

GB 2 119 385 A

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

2119385

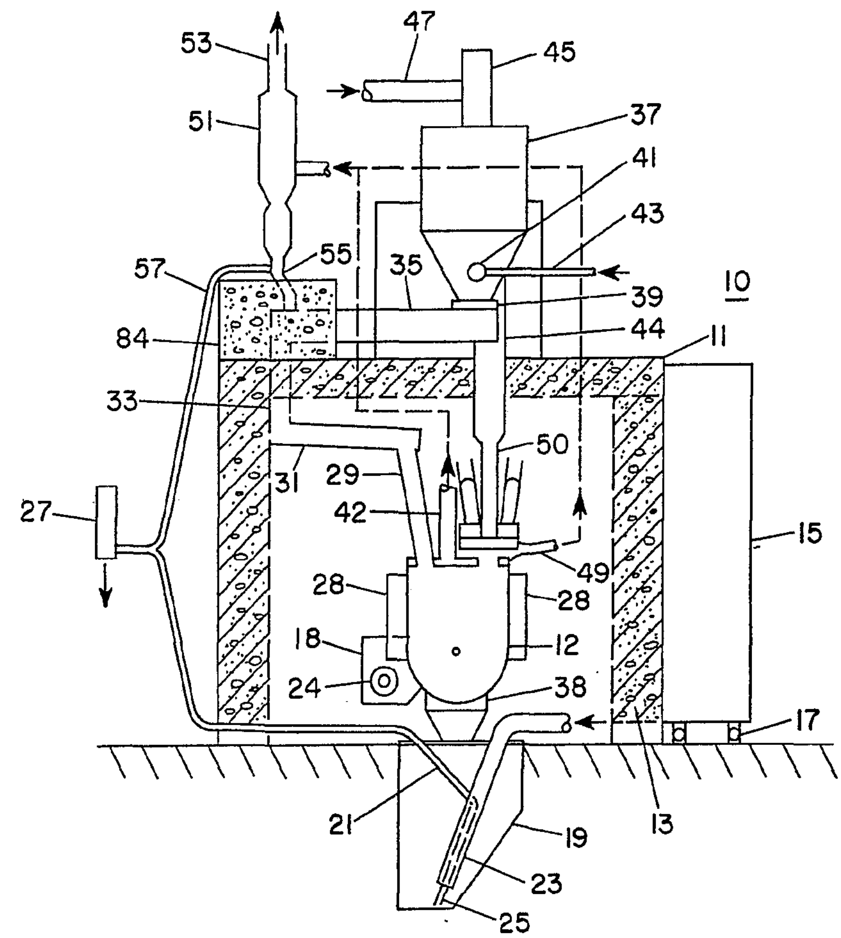


FIG. 1

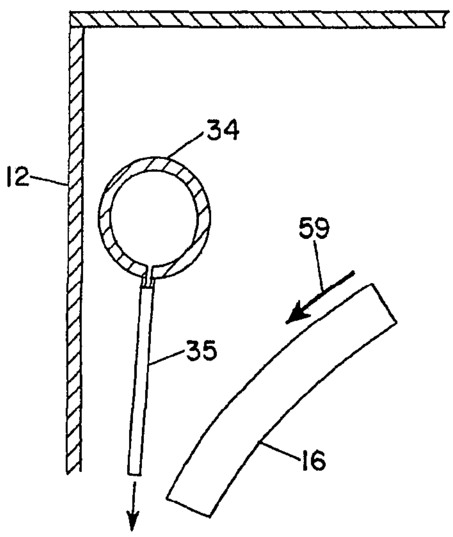


FIG. 2

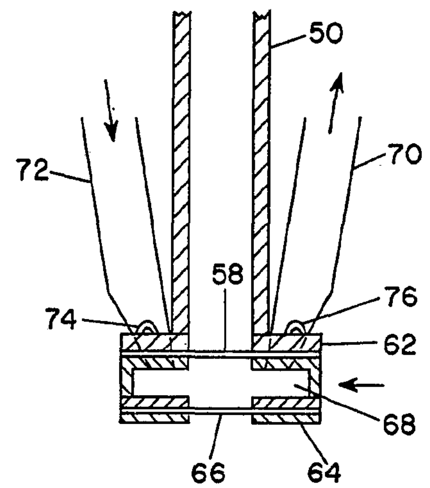
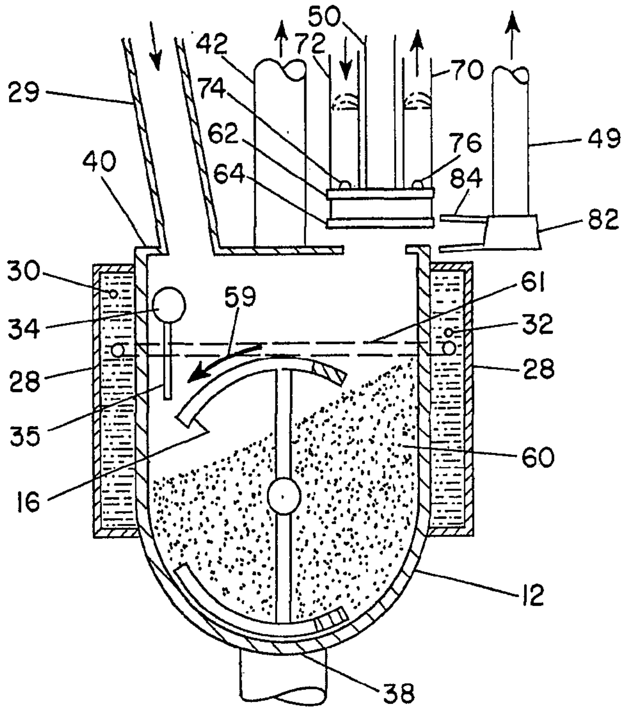
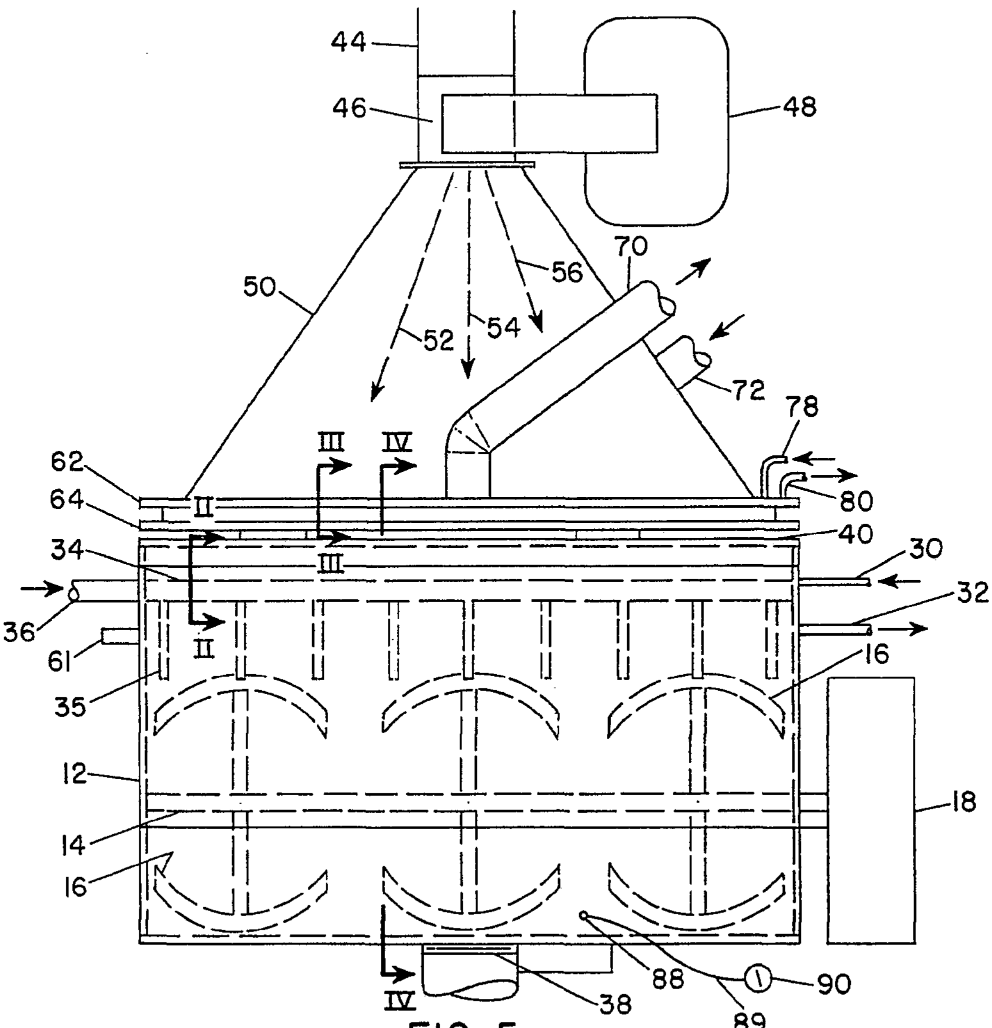


FIG. 3



29
42
72
50
70
74
62
76
49
84
64
82
40
30
61
59
34
32
28
28
35
60
16
12
38

FIG. 4



44
46
48
50
56
70
54
52
72
78
62
III
IV
80
64
II
40
34
III
30
32
36
II
61
16
35
12
18
14
16
88
90
IV
38
89

FIG. 5

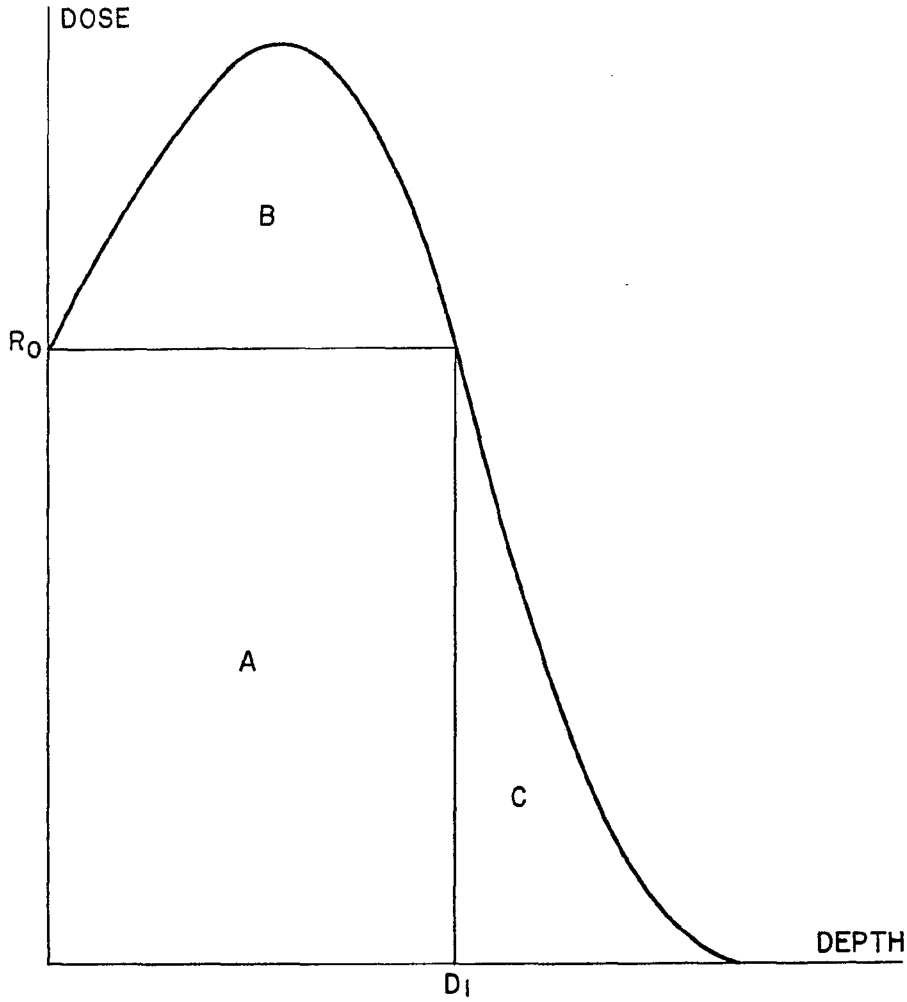


FIG. 6

SPECIFICATION

Apparatus and method for radiation processing of materials

The present invention relates to radiation processing for the degradation of materials and specifically to radiation degradation of polytetrafluoroethylene (PTFE).

U.S. Patent 3,766,031 to Dillon discloses a method for radiation processing of polytetrafluoroethylene, wherein the polytetrafluoroethylene is exposed to radiation and thereafter subjected to comminution to reduce the polytetrafluoroethylene to a fine particle powder. This powder is useful as a dry lubricant, for example, in paints and inks. This and other methods for carrying out this technique generally made use of electron beam or cobalt sources for irradiating the polytetrafluoroethylene. The material being irradiated was arranged in trays and exposed to multiple doses of radiation, approximately 2 to 15 MR per pass, so that the temperature of the material does not rise excessively, thereby to avoid discolouration of the material and the possible generation of noxious gases. The total dose is approximately 35 to 150 MR.

The tray irradiation technique has a radiation utilization efficiency of only approximately 35%. Radiation inefficiencies arise from three factors, which are (1) overscan of trays, (2) gaps between trays and (3) depth-dose characteristics for an electron beam.

The need to ensure complete and uniform irradiation of a tray requires some overscan by the radiation and an efficiency loss of 5 to 15%. Likewise there is usually some space between trays of material which causes a further 10 to 15% loss of efficiency.

The largest efficiency loss arises out of the fact that the dose received by the material varies with the depth of the material. This variation is illustrated in the graph of Figure 6. Typically the dose at the surface, designated R_0, is taken as the nominal dose for the material. Beam energy and/or material depth is adjusted so that an equal dose is obtained at the opposite surface of the material (Depth D). Radiation which passes entirely through the product (Area C) is not utilized. Radiation in Area B in excess of the nominal dose R_0 is likewise not used. This causes further inefficiency, and in some instances may result in undesired properties of the resultant product. Overall this depth-dose characteristic can cause processing inefficiency of up to 50%.

The prior art technique of slow irradiation of material by subsequent exposures to doses of radiation, occasionally coupled with stirring the material between exposures, tends to cause the production of radiation degraded polytetrafluoroethylene powder to be an expensive, inefficient and time consuming operation.

It is an object of the present invention to provide an apparatus and method for more efficiently producing radiation degraded polytetrafluoroethylene.

In accordance with the present invention there is provided an apparatus for radiation processing of chopped flowable solid materials having a high molecular weight to degrade the material to a lower molecular weight and render it grindable into a powder. The apparatus includes a processing vessel for holding the material, a radiation source for supplying radiation to the processing vessel, means for agitating the material during the processing, and cooling means for maintaining the vessel and the material below a selected temperature.

In a preferred embodiment the apparatus includes a dust cover over the vessel and dust collecting means for gathering airborne material particles which accumulate in the dust cover. In connection with the processing, air may be supplied to the material in order to fluidize the material and to additionally cool the material by the flow of air.

The processing vessel is preferably a ribbon blender which includes a vessel and a motor driven stirrer for agitating the contents of the vessel. A preferred radiation source is a source of high energy electrons. The processing vessel can be cooled by a water flow channel surrounding the vessel.

In accordance with another aspect of the invention there is provided a method for processing flowable solid polytetrafluoroethylene material by radiation degradation to reduce the molecular weight of the material and render it grindable into a powder. The method includes exposing the material to radiation, agitating the material during exposure, and maintaining the material at a temperature below 500°F (260°C) during exposure.

In a preferred embodiment the material is fluidized by an air flow during exposure and maintained below 250°F (121°C).

The invention may be put into practice in various ways and one specific embodiment will be described to illustrate the invention with reference to the accompanying drawings in which:

Figure 1 is an end elevation view of a material processing apparatus in accordance with the present invention;

Figure 2 is a partial cross-sectional view of the apparatus of Figure 1 showing an air supply manifold;

Figure 3 is a cross-sectional view of a portion of the electron beam radiation source of the apparatus of Figure 1;

Figure 4 is a cross-sectional view of the processing vessel of the apparatus of Figure 1;

Figure 5 is a side view of the processing vessel of the apparatus of Figure 1; and

Figure 6 is a graph showing how the dose R_0 varies with the depth of the material as discussed above.

Figure 1 is an end elevation view of an apparatus 10 for processing material in accordance with the present invention. Apparatus

10 is particularly useful for performing radiation degradation of polytetrafluoroethylene in order to degrade the material by reducing its molecular weight so to render the material grindable into a powder.

Apparatus 10 includes a processing vessel 12, which comprises the vessel of a ribbon blender, shown in greater detail in Figures 4 and 5. The vessel 12 includes a longitudinal shaft 14 having attached thereto ribbon blending paddles 16 (see Figures 4 and 5). The processing vessel 12 and its associated equipment are enclosed in a radiation chamber 1, made of masonry or other radiation attenuating material. The chamber 11 has an access opening 13 which is closed by a door 15 mounted on rollers 17. The door 15 is provided for equipment access, and other openings, such as a zig-zag hallway, may be provided for personal access. As may be more easily seen by reference to Figures 4 and 5, the paddles are arranged so that the material within the ribbon blender is moved axially back and forth in the longitudinal direction of the shaft 14 when the shaft is continuously rotated in the direction of the arrow 59, and therefore the material undergoes no average axial displacement within the vessel.

The shaft 14 is driven by a reduction gear 18 which is driven by a motor 24. In a typical embodiment the shaft rotates at a speed of approximately 40 revolutions per minute, stirring and agitating the material 60 which has been placed inside the vessel 12.

In one embodiment, the vessel 12 has paddles with a radius of 18 inches (46 cm) and is 72 inches (183 cm) in length. The vessel is provided with a remote control outlet opening 38 in the bottom, for use in draining material after processing. The outlet 38 is arranged above a material receiving chamber 19, so that upon opening it processed material in the vessel 12 will flow into the receiving chamber 19. The material is removed from the receiving chamber by a vacuum apparatus 27 which draws the material into a nozzle 25 and through a conduit 21. An air inlet conduit 23 is arranged around, e.g. concentric to, the nozzle 25 to provide an air supply for removal of the material by the vacuum apparatus. Alternatively a screw conveyor might be used.

In addition, the vessel is provided with a cooling jacket 28 for the flow of cooling water in order to maintain the vessel and its contents at a temperature below approximately 500°F (260°C), preferably below approximately 250°F (121°C). Water is provided through inlet and outlet conduits 30 and 32 and flows between separate portions of the jacket 28 via a conduit 61.

The cooling water is preferably supplied at a temperature which is above the dew point of the surrounding air to avoid condensation. Because the radiation processing of PTFE can release fluorine gas, which combines with water to form hydrofluoric acid, such condensation can cause acid formation and rapid corrosion of the equipment. One method of increasing the temperature of the supply water is to use the cooling water to first cool the power supply of the electron beam apparatus, and thereafter to use the same water at elevated temperature to cool the vessel. Instead of using the same water, a water-to-water heat exchanger can be used. Another technique is to use a conventional water heater to maintain the water temperature above the dew point.

The apparatus of the present invention also includes mechanisms for supplying flowable solid material to the processing vessel 12. This equipment includes an upwardly directed or generally vertical chute 29 leading into the processing vessel and communicating at its upper end with a transversely extending e.g. generally horizontal screw conveyor 31, which is located within the radiation chamber 11. A vertical chute 33 passes through the top of the radiation chamber 11 and connects the interior screw conveyor 31 to an exterior screw conveyor 35. The region surrounding the vertical shaft 33 is provided with an additional radiation shielding structure 84, which may be fabricated out of bricks or the like. The exterior screw conveyor 35 receives granular material to be processed from the bottom of a hopper 37, which is provided with a remote control valve 39 and a vibrator 41 operated by compressed air supplied through a conduit 43. Granular material is supplied to the hopper 37 by a conduit 47 through which material is drawn by a vacuum apparatus 45.

The processing vessel 12 is provided with a cover 40 and a vent conduit 42 through which air is exhausted under lower than atmospheric pressure in order to remove airborne material particles and fluorine gases from the processing vessel so that they do not accumulate and corrode the window of the electron beam source. An additional venting conduit 49, having a lower end 82 with a nozzle 84, arranged near the outlet of the electron beam source, may also be provided.

The conduits 42 and 49 are connected to a cyclone separator 51, which separates airborne material particles from exhaust gases, which are vented through the conduit 53. Particles which accumulate in the separator 51 may be returned to the processing vessel through the conduit 55 during the initial stages of the processing. At later stages of the processing, the material collected by the separator 51 is sufficiently degraded so that it may be transferred through the conduit 57 to the output vacuum apparatus 27.

The electron beam accelerator, which is used to provide a radiation source for the apparatus of Figure 1 includes a vacuum output passage 44 which is connected to a sectoral horn 50 by a beam steering section 46 (not shown in Figure 1; see Figure 5), which is provided with an electro-magnet 48 (see Figure 5). The electron beam source used has an electron acceleration of 1 million volts, and can provide a beam current of up to 100 milli-amperes. The beam steering section 46 causes the beam to oscillate back and forth in the sectoral horn 50 to assume beam paths 52, 54 and 56, as illustrated in Figure 5, thus spreading the radiation along the length of the vessel 12. The electron beam exits from the vacuum portion of the sectoral horn 50 through a primary window 58 and optionally a secondary window 66 respectively, which are shown in detail in Figure 3. The space 68 between the primary and secondary windows is provided with a flow of cooling air through conduits 72 and 70. In addition, conduits 74 and 76 are provided on the flange 62, and possibly also on the flange 64, to provide water cooling of the windows. Cooling water is supplied through conduits 78 and 80 (see Figure 5) and preferably has a temperature above the dew point of the surrounding air to avoid condensation and possible formation of hydrofluoric acid as described above. The windows 58 and 66 comprise thin sheets of titanium, with a thickness of between 0.00075 inches (0.019 mms) and 0.002 inches (0.051 mms). The primary window 58 has a preferred thickness of 0.0015 inches (0.038 mms) in order to support vacuum pressure. The secondary window 66 does not require the same mechanical strength, but a comparable thickness is preferred in order to provide corrosion resistance.

In connection with the processing of materials, such as PTFE in accordance with the present invention, it is desirable to supply a flow of air to the material in the processing apparatus. The air flow serves three functions: (1) the supply of air tends to provide fluidizing of the flowable solid material so that it flows easily when agitated by the stirrer paddles 16; (2) the supply of air tends to promote the degradation reaction, which requires oxygen; and (3) the supply of air into the reaction vessel and out through the conduit 42 (see Figures 1 and 4) tends to promote cooling of the material, as a supplement to the cooling provided by the water jacket 28.

In the embodiment shown in detail in Figure 2, air is provided to the reaction vessel through the manifold 34, which has air outlet passages 35 directed into the material contained in the vessel. Compressed air is supplied through the conduit 36.

In a typical process, flowable solid material such as virgin or scrap polytetrafluoroethylene, in coarse powder or chip form is placed into the vessel 12 and subjected to agitation by the rotation of the stirrers 16 while undergoing irradiation by means of electron beams supplied from the electron source 44. The electron beam from the source 44 is steered in the vacuum passage 46 by alternating currents applied to the electromagnet 48 so that the electron beam diverges in the sectoral horn 50 into paths which are spread out in one angular direction along the length of the vessel 12 as indicated by the beams 52, 54 and 56. The action of the stirrers 16 rotating in the direction 59 tends to circulate the material for uniform irradiation. The electron beams exit from the sectoral horn vacuum through the windows 58 and 66. The irradiation by the electron beam, in combination with stirring action of the stirrer 16 of the ribbon blender causes the degradation of the material to lower its molecular weight from around 5,000,000 to 10,000,000 to less than 1,000,000 and probably less than 100,000. When the molecular weight of the material is thus lowered, it becomes grindable into a powder. In order to promote the reaction by supply of oxygen, provide further cooling of the material during the irradiation process, while the material is undergoing reaction, and in order to make the material more fluid and easier to stir, air may be provided through the conduit 36 into the manifold 34 which has outputs 35 distributed along the length of the vessel 12.

By reason of the agitating action of the stirrers 16, in addition to the air provided through the conduit 34, the process may produce a considerable amount of airborne particles. These particles are constrained within the dust cover 40, which is provided with the outlet conduit 42, which is positively ventilated through the dust collector 51, whereby the recovered material can be recycled into the process vessel or collected as degraded, low molecular weight product through the conduits 55 and 57.

It should be noted as shown in the cross-sectional view of Figure 4 that the action of the stirrers 16 rotating in the direction of arrow 59 will cause the process material 60 build up on one side, for example, the right side, of the reaction vessel 12. In order to provide the most effective radiation treatment, the sectoral horn 50 is directed to a selected region of irradiation at this side of the reaction vessel, so that the electron beams intercept the maximum amount of material to be processed. By directing radiation into the portion of the vessel having a larger depth of material, the efficiency of the process is enhanced, since essentially all of the incident radiation is intercepted by material, rather than passing through without reaction. Further, overradiation which might normally occur for material close to the surface upon which the radiation is incident is avoided by reason of the agitation of the material by the paddles 16.

In order to provide processing of polytetrafluoroethylene in accordance with the method of the present invention using the apparatus of Figure 1, scrap or virgin polytetrafluoroethylene in flowable solid form such as coarse powder or chips, either sintered or unsintered is supplied to the vessel through the chute 29. Typically during processing the volume of the charge of material provided to the reaction vessel is reduced as the bulk density of the material is increased during processing. Processing of a batch of material (approximately 3200 lbs (1455 Kgs)) may use an electron beam accelerated at 1 million volts with a current of 20 to 100 milliamps for six or seven hours. As an alternative to the use of an electron beam accelerator, a radioactive material, such as Cobalt-60 can provide the radiation. Typically only a portion of the full load of material is initially supplied to the vessel 12, for example, one-third to one-half the load. Since the bulk density of PTFE in chip form is generally low, this fills the volume of the vessel. Following initial irradiation additional material can be added because of the increase in bulk density and consequent reduction of the volume of the material during irradiation. After the full load of material has been placed in the vessel 12 irradiation, agitation and cooling is continued until the material receives a dose of 125 to 150 Mrad per pound (275 to 330 Mrad per Kb). During this processing, the temperature of the material is monitored by a thermal sensor 88, which is connected by a wire 89 to a remote meter 90. When the temperature of the material exceeds a selected value, the radiation beam current is reduced. The maximum temperature should be below 500°F (260°C) preferably below 250°F (121°C).

CLAIMS

1. Apparatus for radiation processing of a high-molecular weight, flowable solid material to degrade the said material to lower its molecular weight and render it grindable into a powder, comprising a processing vessel for holding the same material, a radiation source for supplying radiation to a selected region of the said processing vessel, means for agitating the said material during the said processing thereby to move the said material into and out of the said selected region whereby the said material is uniformly irradiated, and cooling means for maintaining the said vessel and the said material below a selected temperature.

2. Apparatus as claimed in Claim 1 in which there is further provided a dust cover over the said vessel, and dust collection means associated with the said dust cover.

3. Apparatus for radiation processing of a high molecular weight, flowable solid material to degrade the said material to lower its molecular weight and render it grindable into a powder, comprising a ribbon blender, including a vessel and a motor driven stirrer for agitating the contents of the said vessel, a radiation source for supplying radiation to a selected region of the said vessel, a water jacket for cooling the said vessel and a dust cover and collector covering the said vessel and adapted to remove airborne material particles therefrom.

4. Apparatus as claimed in any one of Claims 1 to 3 in which the said radiation source comprises a source of high energy electrons and deflection means for distributing the said electrons to the contents of the said vessel.

5. Apparatus as claimed in Claim 4 in which the said source of high energy electrons includes a vacuum passage for the said electrons having an aperture through which electrons pass into the said vessel, wherein the said aperture is provided with primary and secondary aperture windows, and wherein there is provided a flow of air between the said windows.

6. Apparatus as claimed in Claim 4 or Claim 5 in which the said source of high energy electrons includes a vacuum passage for the said electrons having an aperture through which electrons pass into the said vessel, the said aperture being provided with an aperture window, there being provided water cooling for the said window, the said cooling water being provided at a temperature above the dew point of the surrounding air.

7. Apparatus as claimed in any one of Claims 3 to 6 in which the said stirrer causes the said material to accumulate on one side of the said vessel, and wherein the said selected region is on the said one side.

8. Apparatus as claimed in any one of Claims 1 to 7 in which there is provided means for supplying an air flow to the said vessel thereby to cool the said material, fluidize and maintain in a fluidized state the said material and provide oxygen to the said material.

9. Apparatus as claimed in any one of Claims 1 to 8 in which there is further provided a radiation shield surrounding the said processing vessel and the said radiation source.

10. Apparatus as claimed in any one of Claims 1 to 9 in which there is further provided means for supplying flowable solid material through the said radiation shield to the said vessel.

11. Apparatus as claimed in any one of Claims 1 to 10 in which the said processing vessel includes an outlet opening, and wherein there is provided a receiving chamber, communicating with the said outlet openings for receiving processed material from the said vessel.

12. Apparatus as claimed in any one of Claims 1 to 11 in which there is provided means for removing processed material from the said receiving chamber and transporting the said material through the said shield.

13. Apparatus as claimed in Claim 1 substantially as specifically described herein with reference to Figures 1 to 5.

14. A method for processing flowable solid polytetrafluoroethylene material by radiation, to degrade the said material to lower its molecular weight and render it grindable into a powder, comprising supplying the said material to a processing vessel, exposing the said material to radiation, agitating the said material during the said exposure thereby to provide uniform irradiation, and cooling the said material to maintain a temperature below 500°F (260°C) during the said exposure.

15. A method as claimed in Claim 14 in which air is provided to said material to cool said material, fluidize said material, and provide oxygen to said material during said exposure.

16. A method as claimed in Claim 14 or Claim 15 wherein additional material is supplied to the said vessel during the said irradiation.

17. A method as claimed in Claim 14, 15 or 16 in which air is supplied to the said material during irradiation, and wherein the said vessel is vented by negative pressure to remove airborne particles and gases.

18. A method as claimed in Claim 17 in which the said removed material is recovered.

19. A method as claimed in Claim 14 substantially as specifically described herein with reference to the accompanying drawings.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1983. Published by the Patent Office 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.