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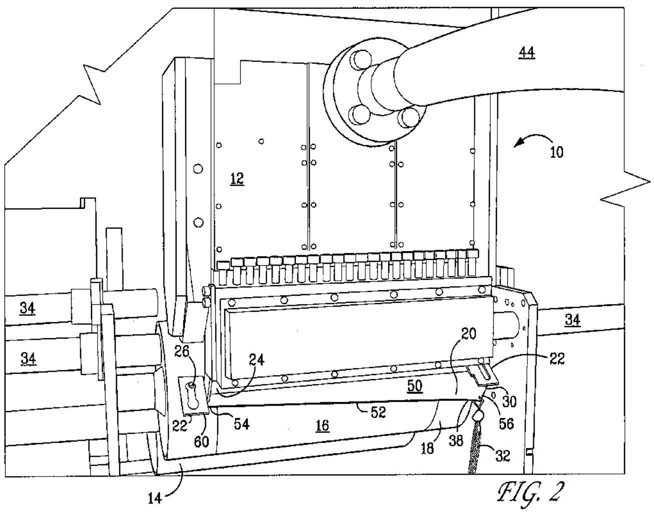

FIG. 2

(57) Abstract: In a system (10) for producing an extrudate (16) of thermoplastic material, the system including an extrusion die (12) having a die outlet (14) that includes a first die lip and a second die lip through which a polymer solution is extruded, and a chill roll (18) for cooling the extrudate, an apparatus (20) for protecting a cooled extrudate. The apparatus includes a plate (50) having a leading edge (52), a first end (54) and a second end (56), the plate having a width that increases from the first end to the second end, along the leading edge(152), and means (60) for attaching the plate adjacent to the first die lip of the extrusion die. A process for making an extrudate of thermoplastic material is also provided.

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Description

APPARATUS AND METHOD FOR PROTECTING EXTRUDATE FROM PROCESS CONDENSATION

FIELD OF THE INVENTION

[0001] This disclosure relates generally to an extrusion apparatus for producing an extrudate and to an apparatus and system for protecting same.

BACKGROUND OF THE INVENTION

[0002] Extrusion dies are used in manufacturing processes to make a variety of goods. Some dies, for example, are used to form thin films, sheets or other elongated shapes of plastic material. Techniques have been developed for melt laminating which involves joining two or more diverse materials (e.g., thermoplastic materials) from separate molten layers under pressure within a die to emerge as a single laminated material. Such processes make use of the laminar flow principle which enables two or more molten layers under proper operating conditions to join in a common flow channel without intermixing at the contacting interfaces. These multiple layer extrusion systems have come into use as a convenient way to provide for the formation of multiple layers of similar or dissimilar materials.

[0003] Various extrusion dies have been produced to extrude multiple layer films. One general configuration of device utilized a first die section which combined the various layers of materials. The combined materials were then flattened and extruded through a second die section. An example of this type of device is illustrated by U.S. Patent No. 5,316,703, incorporated by reference herein in its entirety. This type of device was limited in effectiveness because of the requirement in thin film production that the multi-layer sheet or web have uniform thickness across the width or transverse direction (TD) of the extruded sheet.

[0004] A die assembly can be modular and is typically assembled from a plurality of parts and then set in a die station as an integral device. For example, a die assembly can comprise a first die part and a second die part, which together form the components that allow a fluid to enter the assembly and be properly emitted therefrom. The first die part includes a first lip and the second die part includes a second lip, these lips defining a feed gap therebetween that determines the thickness of the fluid film emitted therefrom.

[0005] Center feed extrusion dies are commonly used in today's plastics industry. A flow stream entering the manifold undergoes flow divergence, as a result of which there occurs a division of the stream into substreams that flow in generally opposite directions to both ends of the manifold. Pressure drop occurs as each substream flows from the centerline of the manifold to its respective manifold end.

[0006] Typically, center feed extrusion dies have a tear drop-shaped, flat manifold, which may be in a form known as a coat hanger manifold, a fish tail manifold, or a T-type manifold. To overcome the pressure drop and produce a substantially equal flow volume of a stream across the stream width, this type of die may further include a flow pressure-compensating preland channel. Also known is a center feed extrusion die having a two stage, flow pressure-compensating, preland channel. This type of apparatus is exemplified in U.S. Patent No. 4,372,739 to Vetter et al. and U.S. Patent No. 5,256,052 to Cloeren.

[0007] A die assembly can have a fixed feed gap or a flexible feed gap. With a fixed feed gap, the lips are not movable relative to each other, so that the thickness of the feed gap will always be the same dimension. With a flexible feed gap, one lip is movable relative to the other lip so as to enable adjustment of the feed gap along the width of the assembly. A flexible feed gap is typically accomplished by assembling the first die part so that it contains a flexible web between its rear portion and its front portion (to which the first lip is attached), as well as means for moving the front portion in localized areas. Movement of the front portion results in the adjustment of the position of the lip relative to the other lip and, thus, the thickness of the feed gap in the relevant localized area.

[0008] In flexible feed gap operations, localized adjustments of the feed gap can usually be accomplished with conventional die assembly designs in order to accommodate a particular run. This is typically accomplished by measuring the thickness of a finished plastic sheet or film across its width downstream from the die lips, readjusting one or more of adjustment bolts, re-measuring the thickness of a finished plastic sheet or film, and so on until the film thickness distribution is within acceptable limits.

[0009] The production of certain specialty films, such as microporous polyolefin membranes have presented additional requirements in the design of extrusion dies for their production. Microporous polyolefin membranes are useful as separators for primary batteries and secondary batteries such as lithium ion secondary batteries, lithium-polymer secondary batteries, nickel-hydrogen secondary batteries, nickel-cadmium secondary batteries, nickel-zinc secondary batteries, silver-zinc secondary batteries, etc.

[0010] As is known, it is desirable for the batteries to have a relatively low shutdown temperature and a relatively high meltdown temperature for improved battery safety, particularly for batteries exposed to high temperatures under operating conditions. Consistent dimensional properties, such as film thickness, are essential to high performing films. A separator with high mechanical strength is desirable for improved battery assembly and fabrication, and for improved durability. The optimization of material compositions, casting and stretching conditions, heat treatment conditions, etc. have been proposed to improve the properties of microporous polyolefin membranes.

[0011] In general, microporous polyolefin membranes consisting essentially of polyethylene (i.e., they contain polyethylene only with no significant presence of other species) have relatively low meltdown temperatures. Accordingly, proposals have been made to provide microporous polyolefin membranes made from mixed resins of polyethylene and polypropylene, and multi-layer, microporous polyolefin membranes having polyethylene layers and polypropylene layers in order to increase meltdown temperature. The use of these mixed resins and the production of multilayer films having layers of differing polyolefins can make the production of films having consistent dimensional properties, such as film thickness, all the more difficult.

[0012] When using a wet extrusion process, a solvent is mixed with the thermoplastic material, which may be a polyolefin, to form a solution. During extrusion, heat is added to the system and gaseous fumes formed and emitted to the system's environment. These fumes, which can contain solvent, liquid paraffin, and the like, can condense to form an oil-like substance under the cooler ambient conditions surrounding the extrusion die, particularly in the region of die outlet and the first chill roll. Further condensation can result at or near the first chill roll due to the cooling of the extrudate and the generally cooler ambient conditions in the region surrounding the first chill roll. The oily condensate can cause surface defects in the extrudate if it lands upon extrudate.

[0013] JP7-216118A discloses a battery separator formed from a porous film comprising polyethylene and polypropylene as indispensable components and having at least two microporous layers each with different polyethylene content. The polyethylene content is 0 to 20% by weight in one microporous layer, 21 to 60% by weight in the other microporous layer, and 2 to 40% by weight in the overall film. The battery separator has relatively high shutdown-starting temperature and mechanical strength.

[0014] WO 2004/089627 discloses a microporous polyolefin membrane made of polyethylene and polypropylene comprising two or more layers, the polypropylene content being more than 50% and 95% or less by mass in at least one surface layer, and the polyethylene content being 50 to 95% by mass in the entire membrane.

[0015] WO 2005/113657 discloses a microporous polyolefin membrane having conventional shutdown properties, meltdown properties, dimensional stability and high-temperature strength. The membrane is made using a polyolefin composition comprising (a) composition comprising lower molecular weight polyethylene and higher molecular weight polyethylene, and (b) polypropylene. This microporous polyolefin membrane is produced by a so-called "wet process".

[0016] Despite these advances in the art, there remains a need for improved extrusion systems capable of producing high quality microporous polyolefin membranes and other films or sheets.

SUMMARY OF THE INVENTION

[0017] In one aspect, provided for use in a system for producing an extrudate comprising polymer and diluent, the system including an extrusion die having a die outlet that includes a first die lip and a second die lip through which a mixture of polymer and diluent is extruded, and a chill roll for cooling the extrudate, an apparatus for protecting a cooled extrudate, the apparatus including a plate having a leading edge, a first end and a second end, the plate having a width that increases from the first end to the second end, along the leading edge; and means for attaching the plate adjacent to the first die lip of the extrusion die.

[0018] In another aspect, a process for producing an extrudate comprising a mixture of polymer and diluent, e.g., thermoplastic material, is also provided. The process includes the steps of combining at least one polymer, e.g., a polyolefin composition, and a diluent (e.g., solvent) to prepare a mixture (e.g., a polyolefin solution), and extruding the mixture through an extrusion die, the extrusion die comprising a die outlet (which can be a slotted die outlet) through which the mixture is extruded, the die outlet comprising a first die lip and a second die lip, cooling the extrudate to form a cooled extrudate, protecting the cooled extrudate from condensate through the use of an apparatus that includes a plate having a leading edge, a first end and a second end, the plate having a width that increases from the first end to the second end, along the leading edge, and means for attaching the plate adjacent to the first die lip of the extrusion die.

[0019] In an exemplary form disclosed herein, the apparatus for protecting a cooled extrudate from condensate includes a guide for directing accumulated condensate oil away from the cooled extrudate. The guide may further include an elongated member of a length sufficient to direct accumulated condensate oil to an oil collection device.

[0020] In a further exemplary form disclosed herein, the means for attaching the plate adjacent to the first die lip of the extrusion die includes a first bracket fastened to the first end of the plate and a second bracket fastened to the second end of the plate.

[0021] In a yet further exemplary form disclosed herein, the means for attaching the plate adjacent to the first die lip of the extrusion die further includes a longitudinal support member, the longitudinal support member fastened to the plate adjacent an edge opposing the leading edge.

[0022] In a still yet further exemplary form disclosed herein, the process further includes the steps of exhausting process gases to minimize condensation, and, consistent with a wet orientation process, removing the solvent from the cooled extrudate to form a solvent-removed cooled extrudate, and drying the solvent-removed cooled extrudate to form the microporous membrane.

[0023] These and other advantages, features and attributes of the disclosed apparatus and system and its advantageous applications and/or uses will be apparent from the detailed description that follows, particularly when read in conjunction with the figures appended hereto.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] FIG. 1 is a perspective view of an apparatus for protecting a cooled extrudate of thermoplastic material, in accordance herewith;

[0025] FIG. 2 is another perspective view of the apparatus for protecting a cooled extrudate of thermoplastic material, in accordance herewith; and

[0026] FIG. 3 is yet another perspective view of the apparatus for protecting a cooled extrudate of thermoplastic material, which also shows a system for handling extrusion process air, in accordance herewith.

DETAILED DESCRIPTION OF THE INVENTION

[0027] Reference is now made to FIGS. 1-3, wherein like numerals are used to designate like parts throughout.

[0028] Referring now to FIGS. 1-3, a system 10 for producing an extrudate is shown. System 10 includes an extrusion die 12 having a die outlet (not shown) which includes a first die lip and a second die lip (also not shown), through which a polymer solution is extruded to form an extrudate 16. As shown in FIG.3, the heated melt stream is supplied to extrusion die 12 by heated hose 44, after filtering through filter 46. Extrudate 16 advances to a first chill roll 18 for cooling the extrudate 16 and may pass to a second chill roll 14 and other additional chill rolls (not shown) for further cooling.

[0029] As those skilled in the art will understand, when using a wet extrusion process for forming extrudate 16, a diluent is mixed with at least one polymer, which may be a polyolefin or polyolefin composition, to form a mixture (e.g., a polyolefin solution). During extrusion, heat is added to the system and gaseous fumes formed and emitted to the system's environment. These fumes, which can contain solvent, liquid paraffin, and the like, can condense to form an oil-like substance under the cooler ambient conditions surrounding die 12, particularly in the region of die outlet 14 and first chill roll 18. Further condensation can result at or near first chill roll 18 due to the cooling of extrudate 16 and the generally cooler ambient conditions in the region surrounding first chill roll 18. The presence of the oily condensate on or near the extrudate can cause surface defects in extrudate 16.

[0030] In order to protect the cooled extrudate 16 from condensate oil that may condense and land upon extrudate 16, an apparatus 20 for protecting cooled extrudate 16 is provided. Apparatus 20 includes a plate 50 having a leading edge 52, a first end

54 and a second end 56. As shown, plate 50 has a width w that increases from first end 54 to second end 56, along leading edge 52. Apparatus 20 further includes means 60 for attaching plate 50 to a region adjacent the first die lip of die outlet 14 of extrusion die 12.

[0031] As shown by reference to FIGS. 1-3, plate 50 of apparatus 20 may be positioned above chill roll 18 and cooled extrudate 16. When positioned in this manner, extrudate 16 is protected from condensate oil that may condense and land upon extrudate 16.

[0032] In one form, apparatus 20 includes a guide 30 for directing accumulated condensate oil away from cooled extrudate 16. In another form, guide 30 may further include an elongated member 32, which may be selected to be of a length sufficient to direct accumulated condensate oil to an oil collection device 36 (see FIG. 3). Elongated member 32 may be a chain, a cord, a hollow tube, or the like and, in the form depicted in FIGS. 1-3, is a chain.

[0033] In one form, guide 30 for directing accumulated oil away from the cooled extrudate 16 further includes a downwardly extending portion 38 of plate 20, formed at second end 56. As shown, elongated member 38 may be attached to downwardly extending portion 38 of plate 20.

[0034] The means for attaching plate 50 adjacent to the first die lip of die outlet 14 of extrusion die 12 may be selected from any number of conventional means, including brackets extending from the die assembly or chill roll frame, welding directly to a portion of the die assembly frame or the like. In one form, means 60 for attaching plate 50 adjacent to the first die lip of die outlet 14 of extrusion die 12 may include a first bracket 22 fastened to first end 54 of plate 50 and a second bracket 22 fastened to second end 56 of plate 50. Means 60 for attaching plate 50 adjacent to the first die lip of die outlet 14 of extrusion die 12 may further include a longitudinal support member 24, longitudinal support member 24 fastened to plate 50 adjacent an edge 58 opposing leading edge 52. In one form, first bracket 22, second bracket 22 and longitudinal support member 24 are fastened to plate 50 with a plurality of bolts 26. Of course, welding or other fastening means may be utilized in the alternative, as those skilled in the art will plainly understand.

[0035] Plate 50 of apparatus 20 may be formed from a variety of materials, so long as the material selected can withstand the extrusion environment, as those skilled in the art will recognize. In one form, plate 50 is a metal plate and may be steel, aluminum or a suitable alloy.

[0036] Referring now to FIG. 3, an air handling system 40 for minimizing the impact of gaseous fumes formed and emitted to the extrusion system's environment is shown. As indicated above, these fumes, which can contain solvent, liquid paraffin, and the like, can condense to form an oil-like substance under the cooler ambient conditions surrounding die 12, particularly in the region of die outlet 14 and first chill roll 18. Air handling system 40 advantageously minimizes their impact.

[0037] Air handling system 40 provides extrusion die 12 with a means for exhausting fumes generated during extrusion. Gaseous fumes generated by extrusion system 10 are evacuated at exhaust hood 46 and transferred away by exhaust hose 48. Additionally, and, as also shown in FIG. 2, fumes generated by extrusion system 10 are evacuated in the region of the die outlet by one or more exhaust tubes 34. As may be appreciated by those skilled in the art, by exhausting at least a portion of the gaseous fumes generated by extrusion system 10, the potential for generating oily condensate that could be deposited on extrudate 16 may be greatly reduced.

[0038] The apparatus and system disclosed herein overcome a difficulty when extruding a mixture of polymer and diluent, e.g., a polyolefin solution, through a die in a variety of processes, including a "wet" microporous membrane film or sheet process. These films and sheets have at least one layer, e.g., single layer comprising polyethylene and/or polypropylene, but the number of layers is not critical. These films and sheets find particular utility in the critical field of battery separators. The invention is compatible with the production of multi-layer films described herein below, which can either be produced using a coextrusion die or be produced using a monolayer die to produce a monolayer film or sheet, with additional layers laminated thereto in a conventional manner. The invention is also compatible with the production of monolayer film.

[0039] In one form, the multi-layer, microporous membrane comprises two layers. The first layer (e.g., the skin, top or upper layer of the membrane) comprises a first microporous layer material, and the second layer (e.g., the bottom or lower or core layer of the membrane) comprises a second microporous layer material. For example, the membrane can have a planar top layer when viewed from above on an axis approximately perpendicular to the transverse and longitudinal (machine) directions of the membrane, with the bottom planar layer hidden from view by the top layer. The extrusion dies described herein are also useful for producing monolayer microporous membranes, e.g., monolayer polyethylene microporous membranes and/or monolayer polyolefin membranes of the type disclosed in PCT Publication WO2007/132942, for example, which is incorporated by reference herein in its entirety.

[0040] In another form, the multi-layer, microporous membrane comprises three or more layers, wherein the outer layers (also called the "surface" or "skin" layers) comprise the first microporous layer material and at least one core or intermediate layer comprises the second microporous layer material. In a related form, where the multi-layer, microporous polyolefin membrane comprises two layers, the first layer consists essentially of the first microporous layer material and the second layer consists essentially of the second microporous layer material. In a related form where the multi-layer, microporous polyolefin membrane comprises three or more layers, the outer layers consist essentially of the first microporous layer material and at least one intermediate layer consists essentially of (or consists of) the second microporous layer material. Such membranes are described in PCT Publication WO2008/016174, US2008/0057388, and US2008/0057389, which are incorporated by reference herein in their entirety.

[0041] Starting materials having utility in the production of the afore-mentioned films and sheets will now be described. Suitable polymers, diluents, and amounts thereof are disclosed in WO2008/016174, US2008/0057388, and US2008/0057389, for example. As will be appreciated by those skilled in the art, the selection of a starting material is not critical as long as an extrusion die and manifold system employing cross flow manifold principles can be applied. In one form, the first and second microporous layer materials contain polyethylene. In one form, the first microporous layer material contains a first polyethylene ("PE-1") having an Mw value of less than about 1×10^6 or a second polyethylene ("UHMWPE-1") having an Mw value of at least about 1×10^6. In one form, the first microporous layer material can contain a first polypropylene ("PP-1"). In one form, the first microporous layer material comprises one of (i) a polyethylene (PE), (ii) an ultra high molecular weight polyethylene (UHMWPE), (iii) PE-1 and PP-1, or (iv) PE-1, UHMWPE-1, and PP-1.

[0042] In one form of the above (ii) and (iv), UHMWPE-1 can preferably have an Mw in the range of from about 1 x 10^6 to about 15 x 10^6 or from about 1 x 10^6 to about 5 x 10^6 or from about 1 x 10^6 to about 3 x 10^6, and preferably contain greater than about 1 wt.%, or about 15 wt.% to 40 wt.%, on the basis of total amount of PE-1 and UHMWPE-1 in order to obtain a microporous layer having a hybrid structure as described in WO2008/016174, and can be at least one of homopolymer or copolymer. In one form of the above (iii) and (iv), PP-1 can be at least one of a homopolymer or copolymer, or can preferably contain no more than about 25 wt.%, on the basis of total amount of the first layer microporous material. In one form, the Mw of polyolefin in the first microporous layer material can have about 1 x 10^6 or less, or in the range of from about 1 x 10^5 to about 1 x 10^6 or from about 2 x 10^5 to about 1 x 10^6 in order to obtain a microporous layer having a hybrid structure defined in the later section. In one form, PE-1 can preferably have an Mw ranging from about 1 x 10^4 to about 5 x 10^5, or from about 2 x 10^5 to about 4 x 10^5, and can be one or more of a high-density polyethylene, a medium-density polyethylene, a branched low-density polyethylene, or a linear low-density polyethylene, and can be at least one of a homopolymer or copolymer.

[0043] In one form, the second microporous layer material comprises one of: (i) a fourth polyethylene having an Mw of at least about 1 x 10^6, (UHMWPE-2), (ii) a third polyethylene having an Mw that is less than 1 x 10^6 and UHMWPE-2 and the fourth polyethylene, wherein the fourth polyethylene is present in an amount of at least about 8% by mass based on the combined mass of the third and fourth polyethylene; (iii) UHMWPE-2 and PP-2, or (iv) PE-2, UHMWPE-2, and PP-2. In one form of the above (ii), (iii) and (iv), UHMWPE-2 can contain at least about 8 wt.%, or at least about 20 wt.%, or at least about 25 wt.%, based on the total amount of UHMWPE-2, PE-2 and PP-2 in order to produce a relatively strong multi-layer, microporous polyolefin membrane. In one form of the above (iii) and (iv), PP-2 can be at least one of a homopolymer or copolymer, and can contain 25 wt.% or less, or in the range of from about 2% to about 15%, or in the range of from about 3% to about 10%, based on the total amount of the second microporous layer material. In one form, preferable PE-2 can be the same as PE-1, but can be selected independently. In one form, preferable UHMWPE-2 can be the same as UHMWPE-1, but can be selected independently.

[0044] In addition to the first, second, third, and fourth polyethylenes and the first and second polypropylenes, each of the first and second layer materials can optionally contain one or more additional polyolefins, and/or a polyethylene wax, e.g., one having an Mw in the range of about 1 x 10^3 to about 1 x 10^4, as described in US2008/0057388.

[0045] In one form, a process for producing a two-layer microporous polyolefin membrane is provided wherein an extrusion die and manifold system of the type disclosed herein is employed. In another form, the microporous polyolefin membrane has at least three layers and is produced through the use of an extrusion die and manifold system of the type disclosed herein. The production of the microporous polyolefin membrane will be mainly described in terms of two-layer and three-layer membrane.

[0046] In one form, a three-layer microporous polyolefin membrane comprises first and third microporous layers constituting the outer layers of the microporous polyolefin membrane and a second (core) layer situated between (and optionally in planar contact with) the first and third layers. In another form, the first and third layers are produced from a first polyolefin solution and the second (core) layer is produced from a second polyolefin solution.

[0047] In one form, a method for producing the multi-layer, microporous polyolefin membrane is provided. The method comprises the steps of (1) combining (e.g., by melt-blending) a first polyolefin composition and at least one diluent (e.g., a membrane-forming solvent) to prepare a first mixture of polyolefin and diluent, e.g., a first polyolefin solution, (2) combining a second polyolefin composition and at least a second diluent (e.g., a second membrane-forming solvent) to prepare a second mixture of polyolefin and diluent, e.g., a second polyolefin solution, (3) extruding the first and second polyolefin solutions through at least one die of the type disclosed herein to form a multi-layer extrudate, (4) optionally cooling the multi-layer extrudate to form a cooled extrudate, (5) removing at least a portion of the membrane-forming solvent from the extrudate or cooled extrudate to form the multilayer membrane, and (6) optimally removing from the membrane at least a portion of any volatile species. An optional stretching step (7), and an optional hot solvent treatment step (8) can be conducted between steps (4) and (5), if desired. After step (6), an optional step (9) of stretching a multi-layer, microporous membrane, an optional heat treatment step (10), an optional cross-linking step with ionizing radiation (11), and an optional hydrophilic treatment step (12), etc., can be conducted.

[0048] The first polyolefin composition comprises polyolefin resins as described above that can be combined, e.g., by dry mixing or melt blending with an appropriate membrane-forming solvent to produce the first polyolefin solution. Optionally, the first polyolefin solution can contain various additives such as one or more antioxidant, fine silicate powder (pore-forming material), etc., as disclosed in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0049] The first and second diluents can be solvents that are liquid at room temperature. Suitable diluents include those described in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0050] In one form, the resins, etc., used to produce to the first polyolefin composition are melt-blended in, e.g., a double screw extruder or mixer. For example, a conventional extruder (or mixer or mixer-extruder) such as a double-screw extruder can be used to combine the resins, etc., to form the first polyolefin composition. The diluent can be added to the polyolefin composition (or alternatively to the resins used to produce the polyolefin composition) at any convenient point in the process. For example, in one form where the first polyolefin composition and the first diluent (membrane solvent) are melt-blended, the solvent can be added to the polyolefin composition (or its components) at any of (i) before starting melt-blending, (ii) during melt blending of the first polyolefin composition, or (iii) after melt-blending, e.g., by supplying the first membrane-forming solvent to the melt-blended or partially melt-blended polyolefin composition in a second extruder or extruder zone located downstream of the extruder zone used to melt-blend the polyolefin composition.

[0051] Suitable methods for combining the polymer and diluent are disclosed in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0052] The amount of the first polyolefin composition in the first polyolefin solution is not critical. In one form, the amount of first polyolefin composition in the first polyolefin solution can range from about 1 wt.% to about 75 wt.%, based on the weight of the polyolefin solution, for example from about 20 wt.% to about 70 wt.%. The remainder of the polyolefin solution can be the solvent. For example, the polyolefin solution can be about 30 wt.% to about 80 wt.% solvent (or diluent) based on the weight of the polyolefin solution.

[0053] The second polyolefin solution can be prepared by the same methods used to prepare the first polyolefin solution. For example, the second polyolefin solution can be prepared by melt-blending a second polyolefin composition with a second membrane-forming solvent.

[0054] The amount of the second polyolefin composition in the second polyolefin solution is not critical. In one form, the amount of second polyolefin composition in the second polyolefin solution can range from about 1 wt.% to about 75 wt.%, based on the weight of the second polyolefin solution, for example from about 20 wt.% to about 70 wt.%. The remainder of the polyolefin solution can be the solvent. For example, the polyolefin solution can be about 30 wt.% to about 80 wt.% solvent (or diluent) based on the weight of the polyolefin solution.

[0055] Advantageously, extrusion dies of the type disclosed herein are used for forming an extrudate that can be co-extruded or laminated. In one form, extrusion dies, which can be adjacent or connected, are used to form the extrudates. The first and second sheet dies are connected to first and second extruders, respectively, where the first extruder contains the first polyolefin solution and the second extruder contains the second polyolefin solution. While not critical, lamination if used is generally easier to accomplish when the extruded first and second polyolefin solution are still at approximately the extrusion temperature.

[0056] In another form, first, second, and third dies are connected to first, second and third extruders, where the first and third dies contain the first polyolefin solutions, and the second die contains the second polyolefin solution. In this form, a laminated extrudate is formed constituting outer layers comprising the extruded first polyolefin solution and one intermediate comprising the extruded second polyolefin solution.

[0057] In yet another form, the first, second, and third dies are connected to first, second, and third extruders, where the second die contains the first polyolefin solution, and the first and third dies contain the second polyolefin solution. In this form, a laminated extrudate is formed constituting outer layers comprising the extruded second polyolefin solution and one intermediate comprising extruded first polyolefin solution.

[0058] The die gaps are generally not critical. For example, extrusion dies of the type disclosed herein can have a die gap of about 0.1 mm to about 5 mm. Die temperature and extruding speed are also non-critical parameters. For example, the dies can be heated to a die temperature ranging from about 140°C to about 250°C during extrusion. The extruding speed can range, for example, from about 0.2 m/minute to about 15 m/minute. The thickness of the layers of the layered extrudate can be independently selected. For example, the resultant sheet can have relatively thick skin or surface layers compared to the thickness of an intermediate layer of the layered extrudate.

[0059] Optionally, the multi-layer extrudate can be cooled. Cooling rate and cooling temperature are not particularly critical. Suitable cooling methods are described in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0060] In one form, at least a portion of the first and second membrane-forming solvents are removed (or displaced) from the multi-layer extrudate in order to form the multi-layer, microporous membrane. Suitable methods for removing the solvents (diluents) are described in WO2008/016174, US2008/0057388, and US2008/0057389, for example. A washing solvent can be used, for example.

[0061] In one form, at least a portion of any remaining volatile species in the membrane (e.g., the washing solvent) are removed. Suitable methods for removing the volatile species are disclosed in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0062] Prior to the step for removing the membrane-forming solvents, the extrudate can be stretched in order to obtain an oriented extrudate. Suitable methods for stretching the extrudate or cooled extrudate are disclosed in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0063] Although it is not required, the extrudate can be treated with a hot solvent as described in WO 2000/20493.

[0064] In one form, the microporous membrane can be stretched at least monoaxially after removal of at least a portion of the diluent. The stretching method selected is not critical, and conventional stretching methods can be used such as by a tenter method, etc. When the extrudate has been stretched as described above the stretching of the dry microporous polyolefin membrane can be called dry-stretching, restretching, or dry-orientation. Suitable stretching methods are disclosed in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0065] The stretching magnification is not critical. For example, the stretching magnification of the microporous membrane can range from about 1.1 fold to about 2.5 or about 1.1 to 2.0 fold in at least one lateral (planar) direction. Biaxial stretching can be used, and the stretching magnification need not by symmetric.

[0066] In one form, the microporous membrane can be heat-treated and/or annealed. The microporous membrane can also be cross-linked if desired [e.g., by ionizing radiation rays such as a-rays, (3-rays, 7-rays, electron beams, etc.)] or can be subjected to a hydrophilic treatment [i.e., a treatment which makes the microporous polyolefin membrane more hydrophilic (e.g., a monomer-grafting treatment, a surfactant treatment, a corona-discharging treatment, etc.)]. Suitable methods for membrane heat treatment, annealing, crosslinking, etc., are described in WO2008/016174, US2008/0057388, and US2008/0057389, for example.

[0067] Alternatively, methods for producing the microporous membrane, such as those described in WO2008/016174 (for multi-layer membranes) and in WO2007/132942 (for monolayer membranes) can also be used.

[0068] While the extrusion has been described in terms of producing two and three-layer extrudates, the extrusion step is not limited thereto. For example, a plurality of dies and/or die assemblies can be used to produce multi-layer extrudates having four or more layers using the principles of the extrusion dies and methods disclosed herein.

[0069] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent and for all jurisdictions in which such incorporation is permitted.

[0070] While the illustrative forms disclosed herein have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside herein, including all features which would be treated as equivalents thereof by those skilled in the art to which this disclosure pertains.

[0071] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

CLAIMS

What Is Claimed Is:

1. In a system for producing an extrudate of polymer and diluent, the system including an extrusion die having a die outlet that includes a first die lip and a second die lip through which a polymer solution is extruded, and a chill roll for cooling the extrudate, an apparatus for protecting a cooled extrudate, the apparatus comprising:

(a) a plate having a leading edge, a first end and a second end, said plate having a width that increases from said first end to said second end, along said leading edge; and

(b) means for attaching said plate adjacent the first die lip of the extrusion die.

2. The apparatus of claim 1, wherein said plate is positioned above the chill roll and cooled extrudate.

3. The apparatus of claims 1 or 2, further comprising a guide for directing accumulated oil away from the cooled extrudate.

4. The apparatus of claim 3, wherein said guide for directing accumulated oil away from the cooled extrudate comprises an elongated member.

5. The apparatus of claim 4, wherein said elongated member is of a length sufficient to direct accumulated oil to an oil collection device.

6. The apparatus of any of claims 3 through 5, wherein said elongated member is a chain.

7. The apparatus of any of claims 3 through 6, wherein said guide for directing accumulated oil away from the cooled extrudate further comprises a downwardly extending portion of said plate formed at said second end thereof.

8. The apparatus of claim 7, wherein said elongated member is attached to said downwardly extending portion of said plate.

9. The apparatus of any preceding claim, wherein said means for attaching said plate adjacent the first die lip of the extrusion die comprises a first bracket fastened to said first end of said plate and a second bracket fastened to said second end of said plate.

10. The apparatus of claim 9, wherein said means for attaching said plate adjacent the first die lip of the extrusion die further comprises a longitudinal support member,

said longitudinal support member fastened to said plate adjacent an edge opposing said leading edge.

11. The apparatus of claims 9 or 10, wherein said first bracket, said second bracket and said longitudinal support member are fastened to said plate with a plurality of bolts.

12. The apparatus of any preceding claim wherein said plate is a metal plate.

13. A process for producing an extrudate of thermoplastic material, comprising the following steps:

(a) combining at least on polymer and at least one diluent to prepare a mixture; and

(b) extruding the mixture through an extrusion die, the extrusion die comprising a die outlet through which a melt stream of the thermoplastic material is extruded, the slotted die outlet comprising a first die lip and a second die lip;

(c) cooling the extrudate to form a cooled extrudate;

(d) protecting the cooled extrudate from condensate formed by step (c) through the use of an apparatus comprising: (i) a plate having a leading edge, a first end and a second end, the plate having a width that increases from the first end to the second end, along the leading edge; and (ii) means for attaching the plate adjacent to the first die lip of the extrusion die.

14. The process of claim 13, wherein the plate is positioned above the chill roll and cooled extrudate.

15. The process of claims 13 or 14, wherein the apparatus further comprises a guide for directing accumulated oil away from the cooled extrudate.

16. The process of any of claims 13 through 15, wherein the guide for directing accumulated oil away from the cooled extrudate comprises an elongated member.

17. The process of claim 16, wherein the elongated member is of a length sufficient to direct accumulated oil to an oil collection device.

18. The process of claims 16 or 17, wherein the elongated member is a chain.

19. The process of any of claims 16 through 18, wherein the guide for directing accumulated oil away from the cooled extrudate further comprises a downwardly extending portion of the plate formed at the second end thereof.

20. The process of any of claims 16 through 19, wherein the elongated member is attached to the downwardly extending portion of the plate.

21. The process of any of claims 13 through 20, wherein the means for attaching the plate adjacent the first die lip of the extrusion die comprises a first bracket fastened to the first end of the plate and a second bracket fastened to the second end of the plate.

22. The process of claim 21, wherein the means for attaching the plate adjacent the first die lip of the extrusion die further comprises a longitudinal support member, the longitudinal support member fastened to the plate adjacent an edge opposing the leading edge.

23. The process of any of claims 13 through 22, wherein the plate is a metal plate.

24. The process of claim 13, further comprising the steps of:

(e) exhausting process gases produced by steps (b) and (c) to minimize condensation;

(f) removing the solvent from the cooled extrudate to form a solvent-removed cooled extrudate; and

(g) drying the solvent-removed cooled extrudate to form the microporous membrane.

25. An apparatus for protecting a cooled polymeric extrudate, comprising:

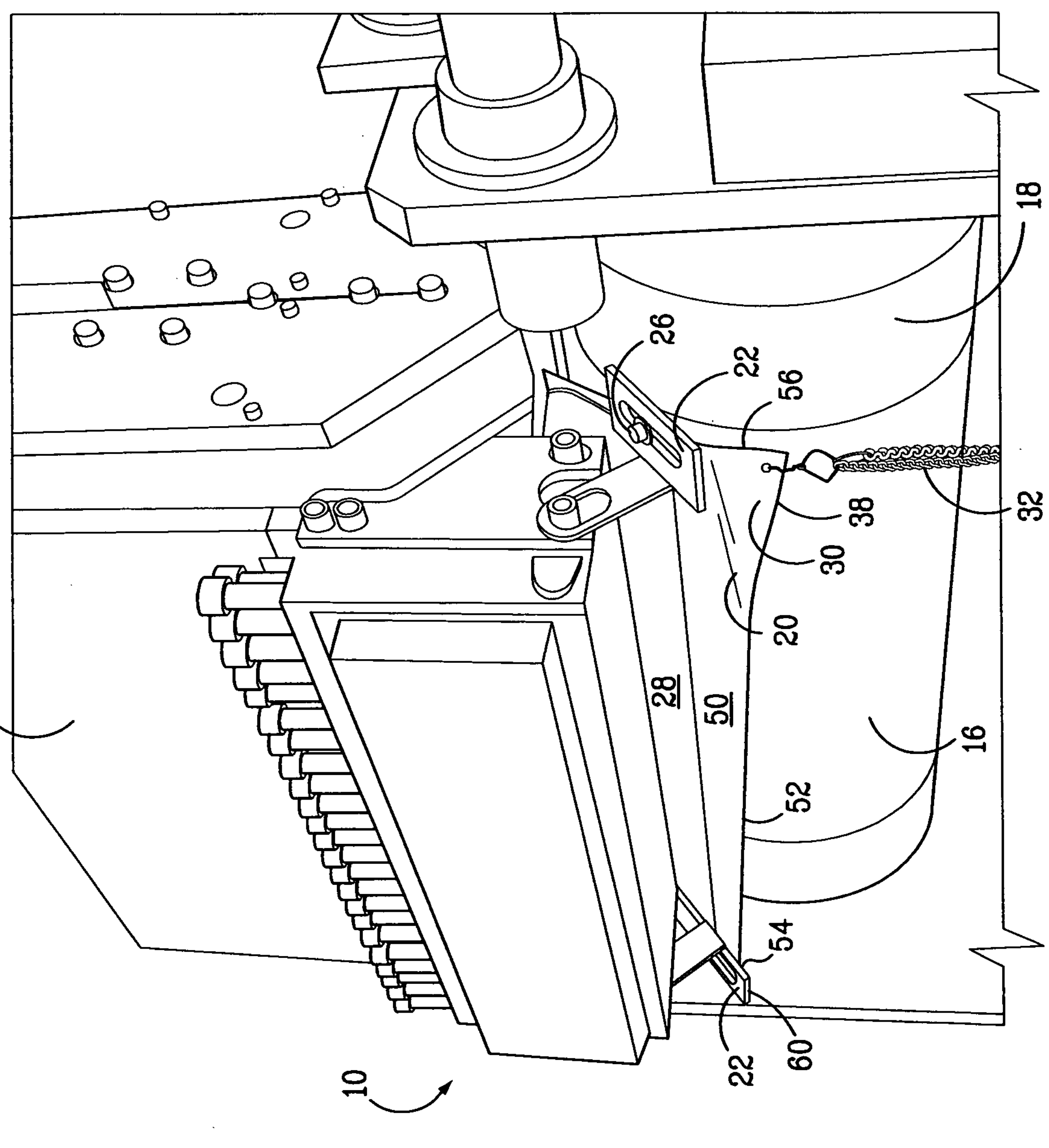
(a) an extrusion die having a die outlet that includes a first die lip and a second die through which a polymer solution is extruded,

(b) a chill roll for cooling the extrudate,

(c) a plate having a leading edge, a first end and a second end, said plate having a width that increases from said first end to said second end, along said leading edge, and

(d) means for attaching said plate adjacent the first die lip of the extrusion die.

FIG. 1



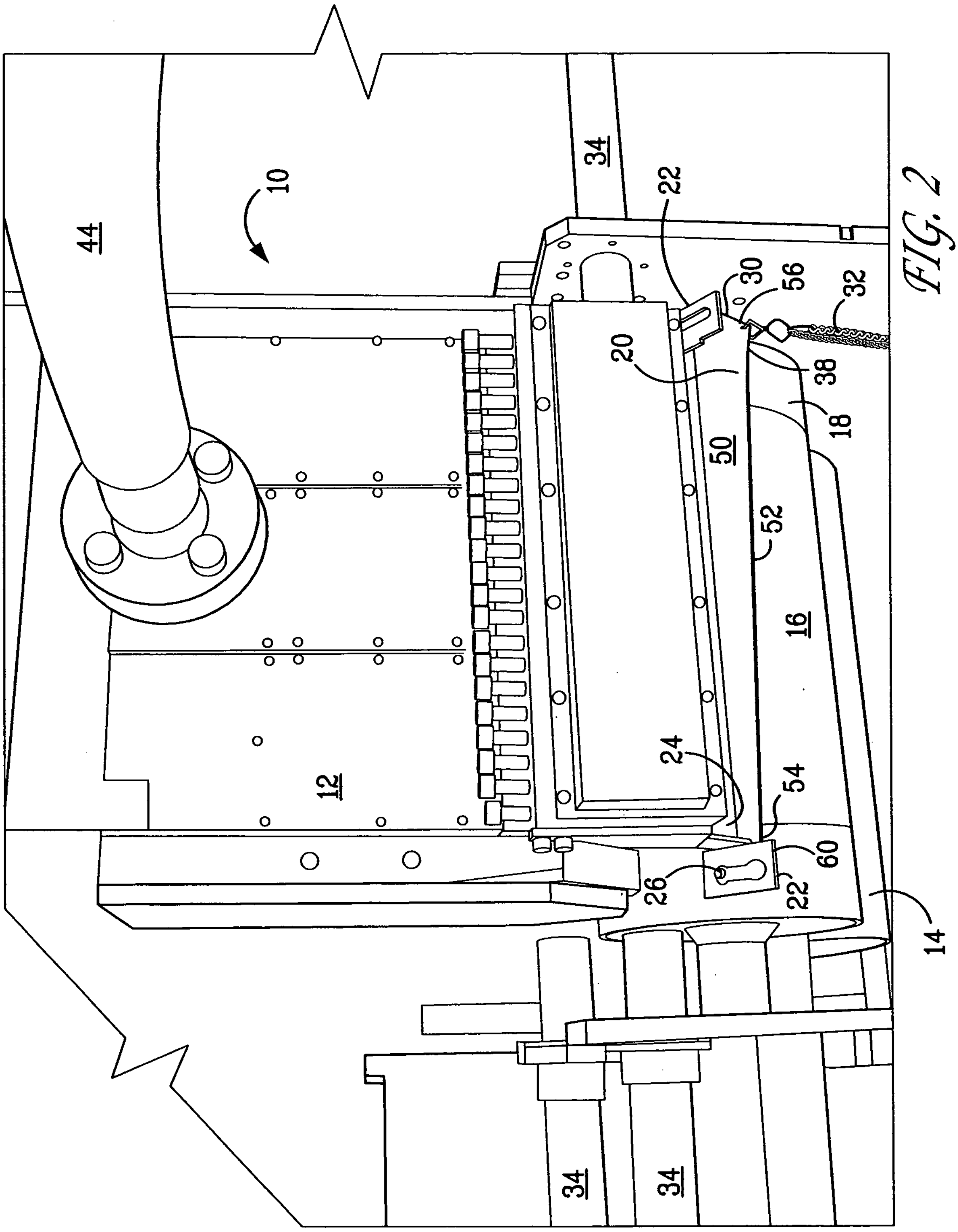


FIG. 2

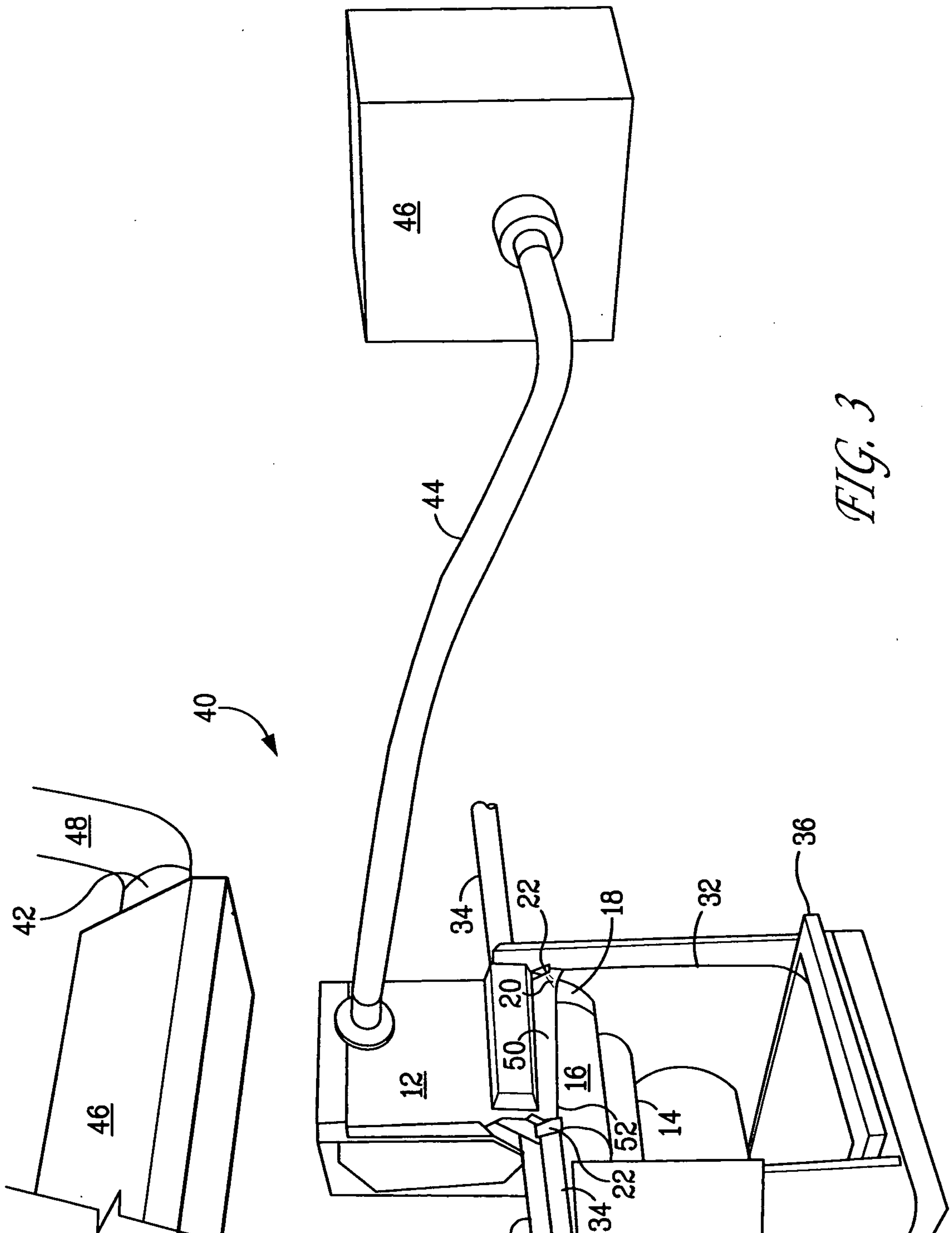


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2008/068129

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29C47/14
ADD. B29C47/08 B29C47/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B29C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 207 708 A (EASTMAN KODAK CO [US]) 7 October 1970 (1970-10-07) page 1; figure 1	1-25
A	DATABASE WPI Week 199225 Thomson Scientific, London, GB; AN 1992-205183 XP002512471 -& JP 04 135823 A (HITACHI CABLE LTD) 11 May 1992 (1992-05-11) abstract	1-25

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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

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

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 January 2009	10/02/2009

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INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2008/068129

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2008/068129

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