(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 July 2011 (28.07.2011)

PCT

(10) International Publication Number
WO 2011/090603 A1

(51) International Patent Classification:
*B29C 47/06* (2006.01) *C09J 7/02* (2006.01)
*B29C 47/14* (2006.01) *B29C 47/88* (2006.01)
*B29C 47/58* (2006.01) *B29C 47/56* (2006.01)

(21) International Application Number:
PCT/US2010/060377

(22) International Filing Date:
15 December 2010 (15.12.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/290,626 29 December 2009 (29.12.2009) US

(71) Applicant *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **AUSEN, Ronald W.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **KOPECKY, William J.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **FLEMING, Danny L.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **YARUSSO, David J.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **BATCH, Gibson L.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **EMSLANDER, Jeffrey O.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **JONZA, James M.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **PASTIRIK, Daniel R.** et al.; 3M Center Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,

*[Continued on next page]*

**(54) Title**: COEXTRUSION DIE AND SYSTEM, METHOD OF MAKING COEXTRUDED ARTICLES AND COEXTRUDED ARTICLES MADE THEREBY

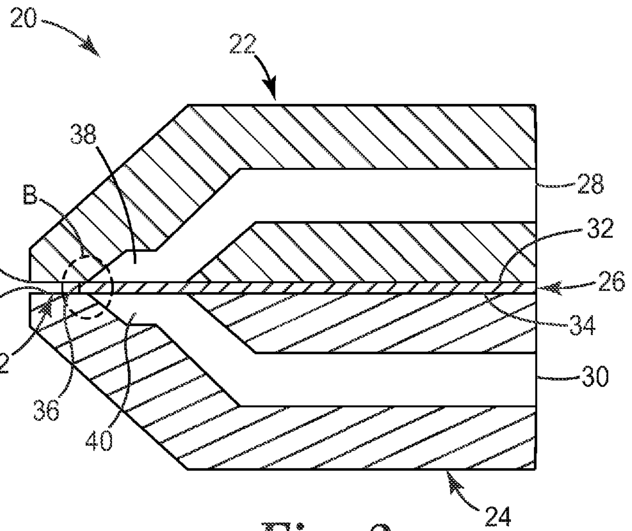


*Fig. 2*

**(57) Abstract**: An extrusion die (20) and method for co-extruding a first molten polymeric material and a second molten polymeric material. The die includes a first die portion (20), a second die portion and a shim separating the first die portion and the second die portion. The shim has a first side and a second side, the first side of the shim forming a boundary of the first die portion and defining a first die cavity (38), the second side of the shim forming a boundary of the second die portion and defining a second die cavity (40). A dispensing edge (36) is provided having a plurality of first and second extrusion openings, a plurality of first feed channels connecting the first die cavity to the first extrusion openings along the dispensing edge, and a plurality of second feed channels connecting the second die cavity to the second extrusion openings along the dispensing edge. The first and second extrusion openings arranged along the dispensing edge to provide an interfacial zone having portions of the first extrusion openings disposed between portions of the second extrusion openings. The die is used in an extrusion system and a method for making a multilayered article.

WO 2011/090603 A1

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17**:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

**Published**:

— *with international search report (Art. 21(3))*

# COEXTRUSION DIE AND SYSTEM, METHOD OF MAKING COEXTRUDED ARTICLES AND COEXTRUDED ARTICLES MADE THEREBY

[0001] The present invention relates to the art of extruding polymeric materials. In particular, the invention relates to coextruding polymeric materials into an article, and more particularly, to coextruding polymeric materials into a multilayered article having a structured interface between the extruded layers. The present invention also relates to an extrusion die for making such an article, to an extrusion system that includes the aforementioned die and to a method of making the aforementioned article by an extrusion process that uses the die.

## BACKGROUND

[0002] The coextrusion of multiple polymeric components into a single layer film is known in the art. Multiple polymeric flow streams have been combined in a die or feedblock in a layered fashion to provide a top to bottom multilayered film. It is also known to provide more complicated coextruded film structures where the film is partitioned, not as coextensive layers in the thickness direction but as stripes along the width dimension of the film. The art has referred to such a process as “side-by-side” coextrusion.

[0003] Improvements are needed in the art of coextruding multiple materials in a layered fashion, including improvements to extrusion devices and to extrusion processes for the manufacture of multilayered films and the like.

## SUMMARY

[0004] The present invention provides improvements in the art of coextrusion to simplify the manufacture of multilayered films and to provide a coextruded structured interface between the extruded layers.

[0005] In one aspect, the present invention provides an extrusion die for co-extruding a first molten polymeric material and a second molten polymeric material, the die comprising: a first die portion; a second die portion; and a shim separating the first die portion and the second die portion, the shim having a first side and a second side, the first side of the shim forming a boundary of the first die portion and defining a first die cavity, the second side of the shim forming a boundary of the second die portion and defining a second die cavity, a dispensing edge comprising a plurality of first and second extrusion openings, a plurality of first feed channels connecting the first die cavity to the first extrusion openings along the dispensing edge, and a plurality of second feed channels connecting the second die cavity to the second extrusion openings along the dispensing edge, the first and second extrusion openings arranged along the dispensing edge to provide: (a) an interfacial zone comprising portions of first extrusion openings disposed between portions of second extrusion openings, (b) a first continuous zone comprising portions of the first extrusion openings arranged in side-by-side relation to each other, and (c) a second continuous zone comprising portions of the second extrusion openings arranged in side-by-side relation to each other, wherein, the interfacial zone is disposed between the first continuous zone and the second continuous zone.

**[0006]** In another aspect, the invention provides an extrusion system for the manufacture of a multilayered film, the system comprising: The extrusion die as described above; a source of first molten polymeric material connected to the extrusion die to feed the first molten polymeric material into the first die cavity; a source of second molten polymeric material connected to the extrusion die to feed the second molten polymeric material into the second die cavity; cooling apparatus positioned to receive a multilayered molten sheet from the extrusion die, the multilayered molten sheet comprising the first and second molten polymeric materials, the cooling apparatus being at a temperature sufficient to at least partially solidify the multilayered molten sheet.

**[0007]** In still another aspect, the invention provides a method of producing an extruded article, the method comprising: providing an extrusion system as described above; feeding the first molten polymeric material from the source of first molten polymeric material into the first die cavity and through the plurality of first extrusion channels, the first molten polymeric material comprising a layer of pressure sensitive adhesive material having first and second major surfaces; extruding the second molten polymeric material from the source of second molten polymeric material through the second die cavity and through the second extrusion channels, the second molten polymeric material comprising a polymer release material having first and second major surfaces; the pressure sensitive adhesive material and the polymer release material exiting the extrusion die through the first and second extrusion openings along the dispensing edge of the die to provide a multilayered extrudate wherein the first major surface of the pressure sensitive adhesive overlays the first major surface of the polymer release material with a structured interface therebetween; and cooling the multilayered extrudate to provide the extruded article in the form of a pressure sensitive adhesive layer and a release liner removably affixed to the adhesive layer.

**[0008]** In still another aspect of the invention, an adhesive article is provided wherein the article comprises: an extruded pressure sensitive adhesive material layer having a first major surface and a second major surface, the first major surface having a microstructure provided by an extrusion die; an extruded release liner comprising a polymeric material layer having a first major surface and a second major surface, the first major surface of the release liner being releasably affixed to the second major surface of the pressure sensitive adhesive material and the first major surface of the release liner having a microstructure complimentary to the microstructure of the second major surface of the pressure sensitive adhesive material layer; wherein, the microstructure on the first major surface of the extruded release liner will retain its form when heated to the melting temperature of the first polymeric material.

**[0009]** The various terms used herein are to be construed as having their common meaning as understood by one of ordinary skill in the art. However, certain terms are expressly defined in order to clarify their meaning within the context of this disclosure.

**[0010]** As used herein, the term “structured interface” refers to the interface between layers of a coextruded material forming a multilayered film wherein the interface is non-planar. In other words, the contours that make up the interface are not all coplanar and often have significant non-planarity. Moreover, the structured interface may present a pattern with features that are measurable on a micro scale, in which case the structured interface may be referred to as a “microstructured” interface.

**[0011]** Terms such as “top”, “bottom”, “upper”, lower”, “under”, “over”, “front”, “back”, “outward”, “inward”, “up” and “down”, and/or “first” and “second” may be used in this disclosure. It will be understood that, unless otherwise noted, those terms are used in their relative sense only. In particular, in some embodiments certain components may be present in interchangeable and/or identical multiples (e.g., pairs). For these components, the designation of "first" and "second" may be applied to the components merely as a matter of convenience in the description of one or more of the embodiments.

**[0012]** The foregoing summary is not intended to describe each and every embodiment or every aspect of the present invention. Those of ordinary skill in the art will more fully understand the invention by considering the description that follows, including the detailed description together with the accompanying drawings and the appended claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0013]** In describing the embodiments of the invention, reference is made to the accompanying drawings which illustrate features that are further described herein. The described features are identified with reference numerals wherein similar reference numerals typically identify similar features. The drawings are provided to facilitate an understanding of the described embodiments and are not to be construed as being to scale. In the various drawings:

**[0014]** Figure 1 is a perspective view of an extrusion die in accordance with one embodiment of the present invention;

**[0015]** Figure 2 is a cross-sectional side view of the extrusion die of Figure 1, taken along section lines 2-2 thereof;

**[0016]** Figure 3 is a top plan view of a shim, shown in isolation, suitable for use in the extrusion die of Figure 1;

**[0017]** Figure 4 is an enlarged perspective view of the area "A" in Figure 3;

**[0018]** Figure 5 is a raised, enlarged, cross-sectional perspective view of the region "B" in Figure 2;

**[0019]** Figures 6A, 6B and 6C are front plan views of different embodiments of a dispensing edge for a shim associated with an extrusion die, according the invention

**[0020]** Figure 7 is a micrograph showing a cross-section of the extruded multilayered film of Example 1;

**[0021]** Figure 8 is a micrograph showing a cross-section of the extruded film of Example 2;

**[0022]** Figure 9 is a micrograph showing a cross-section of the extruded film of Example 3; and

**[0023]** Figure 10 is a micrograph showing a cross-section of the extruded film of Example 4.

## DETAILED DESCRIPTION

**[0024]** The various embodiments of the invention include multizone extrusion dies, systems incorporating such dies, processes using the foregoing extrusion dies and extruded materials resulting from the foregoing processes. In various aspects, the invention facilitates the production or manufacture of multilayered extruded films wherein the interface between the extruded layers is a structured interface, and wherein the structured interface is imparted during the manufacturing process by the multizone extrusion die. In some embodiments, the interface between the layers of film is a microstructured interface.

**[0025]** In some embodiments, multilayered articles can be provided in the form of a layer of a pressure sensitive adhesive coextruded with a polymeric release liner, for example. Along a first major surface, the adhesive may be affixed to a support sheet having, for example, printed graphics on one surface of the support opposite that of the adhesive-coated surface. Along its second major surface, the adhesive is protected by the release liner, and the interface between the adhesive and the liner is microstructured. In the various embodiments, the structured or microstructured interface is created during coextrusion of the adhesive and the release liner. In such an embodiment, the release liner may be removed from the second major surface of the adhesive, and the thus exposed second major adhesive surface may be applied to another support surface (e.g., a wall, billboard, signage, etc.). The microstructured features of the adhesive surface provide air-bleed channels for the escape of air and to avoid the formation of air pockets between the adhesive and the support surface while the adhesive is being married to the display surface.

[0026] In some embodiments of the invention, an extrusion (or coextrusion) die is provided that is configured to coextrude more than one layer of material to form a multilayered sheet material or film having a structured interface between the aforementioned layers. As used herein, the term "coextrusion die" or "extrusion die" will be understood to include a die through which materials (as described herein) may be forced, pressed, pushed, shaped or otherwise directed through the die to provide the described product (e.g., a multilayered sheet material). In some embodiments, the materials may be supplied to the die using one or more extruders (e.g., single or twin screw). In other embodiments, the materials may be supplied through the die using, for example, a grid melter and a gear pump, or other sources of molten material (e.g., molten polymeric material).

[0027] Referring to the Figures, Figure 1 depicts a multizone extrusion die **20** in accordance with one embodiment of the invention. The die **20** includes a first die portion **22** and a second die portion **24**, and a shim **26** disposed between the die portions **22** and **24**. In some embodiments, the shim **26** is metallic. In other embodiments, the shim **26** is made of a ceramic material. The first die portion **22** provides a first zone within the die **20** and a first inlet **28** for receiving a supply of a first molten polymeric material and directing the material into the interior of first die portion **22**. Second die portion **24** provides a second zone that includes a second inlet **30** for directing a supply of a second extrudable polymeric material into the interior of die portion **24**. Both first material inlet **28** and second material inlet **30** are connected to separate sources of extrudable polymeric materials. The inlets **28** and **30** may be made from durable materials and may comprise melt pipes or heated hoses which, in turn, may be connected to pumps and screw extruders (e.g., twin screw and single screw extruders) or other sources of molten polymeric materials.

[0028] Referring to Figure 2, an embodiment of shim **26** is shown which includes a first side **32** and a second side **34** and a leading or dispensing edge **36**. The area designated "**B**" includes a portion of the dispensing edge **36**, described below. Shim **26** is constructed to be positioned between the first die portion **22** and the second die portion **24**. In this construction, first side **32** of shim **26** and first die portion **22** define a first die cavity **38** while second side **34** of shim **26** and second die portion **24** define a second die cavity

**40**. In the embodiment, first and second die portions **22** and **24** include a recessed area **42** in front of dispensing edge **36**. Recessed area **42** extends inside the die **20** from the front surface **44** to the dispensing edge **36**. Recessed area **42** includes land area **43**.

**[0029]** The die cavities **38** and **40** on either side of shim **26** are configured to withstand being filled and pressurized with molten polymeric material. It will be appreciated that the pressure exerted by molten polymeric material will depend on several factors. However, the pressure differential between cavities **38** and **40** should not exceed the physical distortion strength of the shim **26**. In some embodiments, metal shims having thicknesses between about 1 mm and about 2 mm have been strong enough to withstand normal operating pressures. In some embodiments, a thickness of about 1.5 mm is appropriate. Moreover, it will be appreciated that the viscosity of one or both of the polymeric materials may also be manipulated in a known manner as may be needed to assist in controlling the pressure differential between die cavities **38** and **40**.

**[0030]** Referring to Figure 3, a top plan view of shim **26** is shown and will now be described. In the depicted embodiment, dispensing edge **36** is depicted in an optional configuration in which the edge **36** is recessed back from the front edge **45** of the shim to facilitate having the edge **36** offset from the front **44** of die **20**, as previously described. It will be appreciated that the recessed feature of dispensing edge **36** is optional. While such a feature may be desired in some embodiments, like that depicted in Figures 2 and 3, other embodiments of the invention do not require this feature. Through holes **46** may be provided as needed to receive machine bolts or the like therethrough when fastening the components of the die **20** together as an assembly. Through holes **46** may be preformed during the manufacture of the shim **26**, or they may subsequently be drilled at the time the die **20** is assembled.

**[0031]** Referring now to Figure 4, a detailed perspective view is provided of the area "**A**" of Figure 3 to illustrate one embodiment of the extrusion edge **36**. Sufficient extrusion channels are provided to accommodate more than one molten polymeric material. In the depicted embodiment, two sets of inlet grooves are provided within the dispensing edge **36** of the shim **26.** Specifically, first grooves **50** are provided in first side **32** of shim **26**. In the assembled die **20** (see, e.g., Figure 1), first grooves **50** provide the openings for molten polymeric material to travel from first die cavity **38** into first feed channels **60** extending from the first cavity **38** (see Figure 2) to the dispensing edge **36**. Likewise, second grooves **52** are provided in the second side **34** of shim **26** and provide a plurality of openings for molten polymeric material to flow from the second die cavity **40** into second feed channels **64** extending from the die cavity **40** to dispensing edge **36**. First feed channels **60** include side walls **54** and **56** with a joining surface **58** connecting the side walls to one another. Likewise, second feed channels **64** includes side walls **55** and **57** with a joining surface **59** connecting the side walls to one another. In some embodiments, the joining surface of each of the feed channels and openings slope at an angle, typically an acute angle, toward the dispensing edge **36**.

**[0032]** First grooves **50** extend from the upper or top side of the shim **26** forming a plurality of first feed channels **60** which terminate along the dispensing edge **36** at first openings **62**. Second grooves **52** extend from the lower or bottom side of the shim **26** forming a plurality of second feed channels **64** connected to second openings **66** along the dispensing edge **36**. The first grooves **50** and first feed channels **60** are disposed so that each first feed channel **60** is disposed between adjacent second feed channels **64**, and vice versa. Similarly, first openings **62** alternate in frequency with second openings **66** along the length of dispensing edge **36**.

**[0033]** Referring to Figure 5, a partial view of shim **26** is shown, in cross section, retained between first die portion **22** and second die portion **24**. Shim **26** is retained between die portions **22** and **24** so as to form a seal around the dispensing edge **36** to prevent intermixing of molten polymeric materials flowing through die cavities **38** and **40** before the molten materials are dispensed from openings **62** and **66** along dispensing edge **36**. During an extrusion operation using the die **20**, a first molten polymeric material is disposed in first die cavity **38**. Under pressure, the material is forced or pushed in direction **D1** through the first cavity to first grooves **50**. The first molten polymeric material moves through the grooves **50** into the first feed channels **60** and ultimately through first openings **62** along the dispensing edge **36**. Similarly, molten second polymeric material is moved into the second cavity **40**. Under pressure, the second material is moved in direction **D2** through the second cavity to second grooves **52**. The second molten polymeric material moves through the grooves **52** into the second feed channels **64** and ultimately through second openings **66** along the dispensing edge **36**.

**[0034]** Referring to Figure 6, alternate configurations are depicted for the dispensing edge of shim **26**. Figure 6A is a front view of a portion of one embodiment for configuring the dispensing edge of the shim **26**. As can be seen, dispensing edge **136** is similar to edge **36** of Figure 4. In the embodiment of Figure 6A, first openings **162** and second openings **166** are substantially parallel to one another, and each first opening **162** extends downwardly and terminates at an edge **158** while each second opening **166** extends upwardly, as depicted, and terminates at an edge **159**. First and second openings **162** and **166** extend slightly past one another so that each of the openings can be characterized as partially overlapping, with the overlapping portions of the openings falling within an "interfacial zone," designated in the Figure as the area **172**. The remaining portions of first and second openings **162** and **166** are outside of the interfacial zone **172** with the non-overlapping portions of first openings **162** forming a first continuous zone **174** and the non-overlapping portions of second openings **166** forming a second continuous zone **176**. During an extrusion operation, first and second molten polymeric materials are forced through the openings **162** and **166** as molten "fingers" of material. These fingers of molten material will expand or swell in a known manner upon exiting openings **162** and **166** along the dispensing edge **136**. The portions of materials extruded though the openings **162** and **166** within the interfacial zone **172** will result in an overlapping structure comprised of portions of first molten polymeric material disposed between portions of the second molten polymeric material. The portions of materials extruded though the openings **162** and **166** outside of the interfacial zone and in the first continuous zone **174** and second continuous zone **176** will result in continuous areas of first material and continuous areas of second material on either side of the interfacial structure. The resulting product is a two layered sheet of first material and second material overlying one another and sharing a common structured interface. As described, the structured interface is the result of the portions of first and second materials that pass through interfacial zone **172**.

**[0035]** Referring to Figure 6B, another embodiment of a dispensing edge **236** for inclusion in shim **26** is shown. First openings **262** and second openings **266** are substantially parallel to one another but have unequal widths (e.g., their corresponding side walls are not spaced apart the same distance). Each first opening **262** extends downwardly and terminates at edge **258** while each second opening **266** extends upwardly and terminates at edge **259**. First and second openings **262** and **266** extend slightly past one another so that each of the overlapping portions of openings **262** and **266** can be characterized as falling within an "interfacial zone," designated as the area **272**. The portions of materials extruded though the openings **262** and **266** outside of the interfacial zone in the first continuous zone **274** and/or the second continuous zone **276** result in continuous areas of first material and continuous areas of second material, respectively, on either side of the structured interface. The resulting product is a two layered sheet of first material and second material overlying one another and sharing a common structured interface. As described, the structured interface is the result of the portions of first and second materials that pass through interfacial zone **272**.

**[0036]** Referring to Figure 6C, still another embodiment of a dispensing edge **336** suitable for use in shim **26** is shown. First openings **362** are provided with side walls that are perpendicular to the corresponding side of the shim **26** from which they are cut. Second openings **366** have been cut so as to form side walls that taper at a non-right angle to the corresponding side of the shim **26**. Each first opening **362** extends downwardly, as shown in the Figure, and terminates at edge **358** while each second opening **366** extends upwardly, as depicted, and terminates at edge **359**. First and second openings **362** and **366** extend slightly past one another so that each of the overlapping portions of openings **362** and **366** can be characterized as falling within an "interfacial zone" **372**. The portions of materials extruded though the openings **362** and **366** outside of the interfacial zone and in the first continuous zone **374** and second continuous zone **376** will result in continuous areas of first material and continuous areas of second material on either side of the structured interface. The resulting product is a two layered sheet of first material and second material overlying one another and sharing a common structured interface. As described, the structured interface is the result of the portions of first and second materials that pass through interfacial zone **372**.

**[0037]** As shown in the embodiments of Figures 6A-6C, the profiles of the first and second openings along the dispensing edge and their corresponding feed channels can be provided with identical configurations or they may be configured differently. The side walls of the first and second feed channels can be parallel to each other, or they can be angled (e.g., an acute, right or obtuse angle) with respect to each other. In addition, the side walls of the first feed channels can be perpendicular or they can be oriented at an angle (other than a right angle) with respect to the first side of the shim, or the side walls of the first channels can be formed so as to taper outwardly from the joining surfaces to the first side and the dispensing edge of the shim (i.e., the distance between the side walls adjacent the joining surface can be smaller than the distance between the side walls either adjacent the first side of the shim, adjacent the dispensing edge, or both). Likewise, the side walls of the second channels can be perpendicular or they can be oriented at an angle (other than a right angle) with respect to the second side of the shim, or the side walls of the second channels can be formed so as to taper out from their joining surfaces to the second side and the dispensing edge of the shim (i.e., the distance between the side walls adjacent the joining surface can be smaller than the distance between the side walls either adjacent the second side of the shim, adjacent the dispensing edge, or both).

**[0038]** The side walls of both sets of feed channels can be perpendicular to or they can taper out to their corresponding side of the shim and the dispensing edge, or one set of channels can be perpendicular and the other set tapered. The depths of the first and second feed channels can also be similar or different. The use of slanted feed channels will create slanted zones, relative to the plane of the extrudate (e.g., a film).

**[0039]** Depending on the desired configuration of the structured interface in the multilayered extrudate, it is typically desirable for the first openings of the first feed channels to extend from a first side of the shim part way (e.g., not all the way) toward the second side of the shim. Similarly, the second openings of the second feed channels ought to extend from the second side of the shim part way toward the first side of the shim. In such a construction, the dispensing edge of the shim is provided with an interfacial zone for the creation of a structured interface, as previously described. The degree of overlap between the first and second openings can be varied somewhat, and the configurations, dimensions and orientation of the openings may be varied in order to provide the structured interface suitable for a particular article. The present invention allows for the use of relatively narrow exit openings. For example, each exit opening of either the first or second channels can have a maximum width dimension (i.e., the maximum distance between opposite side walls of the channel at the exit opening) of less than or equal to about 1.5 mm (1500 micrometers). Larger channel width dimensions can also be used in accordance with the various embodiments of the present invention. The resistance to flowing a polymeric material through a channel can increase as the reciprocal of the third power of the channel width. This resistance can limit, as a practical matter, the effective minimum dimensions of the channels. As a result, each of the channels may have a minimum width dimension (i.e., the minimum distance between opposite side walls of the channel at the exit opening) of about 50 micrometers, or possibly as low as about 25 micrometers. It may be possible to extrude with even smaller channel width dimensions by using heat or radiation curable polymeric materials, since such materials typically have relatively lower viscosities than thermoplastic extrudable polymeric materials. In some embodiments, the dispensing edge may be provided as a non-planar surface. In some embodiments, the dispensing edge is chamfered at one or both of its edges to assist in the formation of a continuous layer of one or both of the first and second molten polymeric materials.

**[0040]** In each of the embodiments of the dispensing edges illustrated in Figures 6A to 6C, each of the dispensing edges are affixed to a shim which, in use, serves to separate two molten polymeric materials during the extrusion process as the materials travel through the chambers of the die **20** and to the dispensing edge **36**. The foregoing embodiments are not to be construed as limiting but are representative of the degree to which the first and second exit openings overlap each other in order to provide a structured interface between the layers of extruded materials. The particular configuration of the structured or microstructured interface can depend on a variety of factors including the degree of overlap between the first and second openings (e.g., the relative size of the interfacial zone on the die face), the configuration or shapes of the exit openings on the dispensing edge and the properties of the materials being extruded, for example.

**[0041]** The foregoing embodiments of a die may be manufactured in a known manner, With regard to the manufacture of a dispensing edge for an extrusion shim (e.g., shim **26** in Figure 3), the grooves, feed channels and exit openings may be made using, for example, wire electrical discharge machining (EDM) or other methods of machining techniques such as laser, e-beam, or diamond machining.

**[0042]** In the use of the foregoing die, any of a variety of extrudable polymeric materials can be used. In addition to conventional extrudable thermoplastic polymeric materials, the present invention may also be used to coextrude polymeric materials that can be crosslinked. For example, either or both of the first and second extrudable polymeric materials may comprise curable resin. When a heat curable resin is used, the die **20** can be heated to initiate the curing process as well as to adjust the viscosity of the polymeric material and/or the pressure in the corresponding die cavities (e.g., cavities **38** and **40**).

**[0043]** In embodiments of the invention, a system for the manufacture of multilayered sheets is provided that includes sources of the first and second molten polymeric materials to provide the polymeric materials to the extrusion die. In some embodiments, sources of the first and second molten polymeric materials are first and second extruders which are equipped to process different polymer materials. Both extruders are connected to the above described die **20** so that the first extruder provides a first molten polymeric material to the first die zone or cavity **38** and second extruder provides a second molten polymeric material to the second die zone or die cavity **40**. The operation and configuration of such a system will be known to those of ordinary skill in the art. Suitable extruders will be capable of processing polymeric and monomeric materials as well as additives, solvents and the like in order to provide first and second molten polymeric materials that may be processed through the die **20** as previously described. Either or both of the extruders may comprise a plurality of heated zones as well as a hopper to direct components of the polymeric materials into the extruders in a known manner. In various embodiments, either single screw extruders or twin screw extruders may be used.

**[0044]** In the aforementioned system, die **20** is positioned to receive feeds of molten polymeric materials coming from both extruders and to maintain the feeds as separate streams, each stream passing through one of the die cavities **38** and **40** and into the dispensing edge **36** and feed channels **60** and **64**, as previously described. The two molten polymeric materials are extruded through the multizone die **20** in two streams which adhere to one another to from a multilayered sheet having two distinct layers, each layer formed by one of the molten polymeric materials. As mentioned, the interface between the layers is structured as a direct result of the configuration of the openings (e.g., openings **62** and **66**) and the degree to which the openings overlap one another within the interfacial zone (e.g., zone **172**, Figure 6A). It will be appreciated that other embodiments, the system can includes other means for the delivery of molten polymeric materials to the extrusion die. In some embodiments, one or more grid melters and pumps will deliver molten polymeric materials to the extrusion die **20**. In some embodiments, a single extruder may supply one of the molten materials to the die while another means (e.g., a grid melter and pump) may be used for the delivery of the other molten material. It will be understood that the inclusion of single or double screw extruders as an initial source of material is a matter of design choice depending on the materials being used and other criteria familiar to those of ordinary skill in the art.

**[0045]** The extruded multilayered sheet is cooled upon exiting the die **20**, and the sheet material may then be further processed or, for example, wound up onto a roll for storage or further processing at a later time. Cooling of the material may be accomplished on a chill roll or the like positioned to receive the multilayered extrudate as it exits the die. In other embodiments, the molten material is cooled on a series of cooling rolls or in a water bath, for example.

**[0046]** In some embodiments, the molten polymeric materials are a polymer-containing adhesive, such as a pressure sensitive adhesive, and a release liner. In embodiments of the invention that comprise the coextrusion of a pressure sensitive adhesive and a release liner, any of a variety of suitable adhesive compositions may be used including without limitation those based on rubbers, thermoplastic elastomers, polyvinyl ethers, poly-alpha-olefins, polyacrylates and/or methacrylates, silicones and the like.

**[0047]** In some embodiments, the pressure adhesive is an acrylate adhesive formed by reaction of one or more acrylate or methacrylate monomer(s) and acrylic acid. In one embodiment, the acrylate adhesive comprises a polymer that is the reaction product of acrylic acid and 2-ethylhexyl acrylate. Suitable monomers can be selected from the group acrylic acid, butyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, isononyl acrylate, n-butyl acrylate, 2-methyl-butyl acrylate, methyl acrylate, ethyl acrylate, acrylonitrile, methyl methacrylate, trimethylolpropane triacrylate (TMPTA), vinyl acetate, N-vinyl pyrrolidone, methacrylamide, and combinations of two or more of the foregoing. In other embodiments, the adhesive is a block copolymer such as, for example, styrene-isoprene block copolymer or an ethylene/methacrylic acid. The combination of block copolymers may include di-block, tri-block, tetra-block and higher order (so called star-block) copolymers.

**[0048]** In addition to the described embodiments of base adhesive resin, those of ordinary skill in the art will appreciate that tackifying resins and other additives may be added to the adhesive formulation to adjust initial tack, adhesive strength, performance over a desired temperature range, dispensability or durability. Some examples of tackifiers include rosin ester resins, aromatic hydrocarbon resins, aliphatic hydrocarbon resins, and terpene resins. Oils, plasticizers, fillers, antioxidants, ultraviolet stabilizers, flame retardants and curing agents are examples of other classes of additives.

**[0049]** Release liners may be made from known materials suitable for such an application such as, for example, plastic materials such as polyolefins and, more specifically, polypropylene, polyethylene. Suitable polyethylene may be a high density polyethylene (HDPE), a low density polyethylene (LDPE), an ultra-low density polyethylene, or random or block copolymers of ethylene, propylene, butane, hexane and/or octene. Suitable polypropylenes include homopolymers and copolymers with ethylene, butane, hexane, and/or octene,

**[0050]** Another suitable class of release materials are fluoropolymers such as homopolymers and copolymers chosen from vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropylene, perfluoromethyl vinyl ether, combinations of the foregoing and possibly also containing ethylene, propylene, butane, hexane, octene, or minor amounts of other vinyl monomers.

**[0051]** Yet another suitable class of release materials are silicones. These materials contain -O-Si- backbones. Side groups may include methyl, ethyl and longer alkyl, fluoroalkyl, phenyl or vinyl moieties. Additionally, silicone block copolymers may also be useful.

**[0052]** In embodiment, the inventions provides a pressure sensitive adhesive and a release liner wherein the coextrusion process of the invention provides a structured interface in which the release layer retains a structured or microstructured configuration at its normal melting point. Consequently, coextrusion enables a temperature tolerance for the release layer that is not witnessed in an embossing process, for example. Moreover, coextrusion avoids the need for additional steps in the manufacture of an adhesive article as described herein and, with the manufacture of an appropriate die, provides a relatively fast and inexpensive manufacturing process for structured or microstructured pressure sensitive adhesive articles with a release liners. In some embodiments, the foregoing embodiments of the invention are especially useful in the manufacture of acrylate adhesives and polyethylene release liners wherein the structured surface is a microstructured surface that provides air bleed channels for the escape of air while the pressure sensitive adhesive is married with a display surface or the like.

**[0053]** Additionally, any of the foregoing adhesive materials and/or the release liner materials may be further reinforced with another support layer, as known by those of ordinary skill in the art. Suitable materials for supporting the adhesive may be selected from any of a variety of sheet materials such as woven materials, non-woven materials, polymeric sheets, man-made and natural fabrics, paper, or the like. In some embodiments, the support is a sheet material that is capable of receiving printed letters and images on the major surface of the adhesive opposite the structured interface. In some embodiments, the adhesive layer is a pressure sensitive adhesive, and the support for the adhesive includes printed words or images on the major surface of the support opposite the structured interface. In such a construction, with the release layer removed, the structured surface of the adhesive is exposed and may be applied to a suitable display surface (e.g., a wall, billboard or the like). In the application of the adhesive to a display surface, the structured surface of the adhesive provides air bleed channels which provide a pathway for air to escape while the adhesive is being married to the display surface. In such a construction, the entrapment of air bubbles or air pockets between the adhesive and the display surface is avoided, and the printed words or images on the non-adhesive side of the support can be displayed and viewed as originally intended, i.e., on a smooth flat surface. Application of a support layer to the adhesive or to the liner may be made in a continuous or in a non-continuous manner. Suitable support materials for the release liner include paper, other polymer materials, fabrics, woven materials, nonwoven materials and the like.

[0054] In addition to graphical displays comprising the foregoing pressure sensitive adhesive and release liner, embodiments of the invention may be used in the preparation of other multilayered sheet-like constructions such as drag reduction films applied to airplanes, boats, automobiles, wind or water turbines. Abrasion resistant films for wind turbine blades, automobiles and other vehicles as well as rollgoods, flooring and roofing products may also be prepared according to one or more embodiments of the invention.

## EXAMPLES

[0055] Specific detailed embodiments are further provided in the following non-limiting Examples.

**Shim Preparation:**

[0056] A shim similar to that shown in Figure 3 was manufactured from 1.5 mm thick stainless steel metal shim stock. Two sets of grooves, feed channels (micro-channels) and openings were machined into the dispensing edge of the shim using conventional wire electron discharge machining (EDM) techniques. The first set of feed channels, in the upper/top side of the shim, had a length of 1600 microns measured in the direction of polymer flow and a width of 87.5 microns with openings extending 1050 microns across the width of the dispensing edge of the shim. The second set of feed channels, in the lower/bottom side of the shim, had a length of 1600 microns measured in the direction of polymer flow and a width of 125 microns and included openings that extended 825 microns across the width of the dispensing edge of the shim. The first set of openings alternated with the second set of openings across the dispensing edge of the shim with a spacing of 70 microns between each opening, and each of the feed channels and openings were separated from adjacent channels and openings by a foil barrier. The shim was used in an extrusion die by positioning the shim between two die halves with a sealing surface that extended back from the dispensing edge of the shim by a distance of about 1000 microns

**Example 1**

**[0057]** A coextruded film was prepared using the shim described above and the following procedure. A 32-mm single screw extruder (3:1 L/D, water-cooled feed throat) was used to melt and extrude a low density polyethylene (INFUSE D9807, 15 MI, from Dow Chemical Co., Midland, MI) into a first manifold of a dual-manifold extrusion die. The polyethylene was pigmented blue using 2% by weight of a blue color concentrate. A flow rate of 1.2 kg/hr was used. The melt temperature was maintained at 190°C. A second 32-mm single screw extruder (3:1 L/D, water-cooled feed throat) was used to melt and extrude an acrylate adhesive into a second manifold of a dual-manifold extrusion die. The acrylate adhesive consisted of a pre-polymerized blend of 87.5% by weight ethyl hexyl acrylate and 12.5% acrylic acid. The adhesive was melted in a Bonnot adhesive pump set at 175°C (Bonnot Model 2WPKR, 50 mm, from Bonnot Manufacturing, Green, Ohio) and then injected into the extruder just after the feed throat. A flow rate of 2.1 kg/hr was used. The melt temperature was maintained at 190°C. The extrudates from the extruders were fed to a dual-manifold die maintained at 204°C and fitted with the shim described above. The polyethylene was used to feed the first manifold of the die which supplied material to the first set of grooves in the upper/top side of the shim. The acrylate adhesive was used to feed the second manifold of the die which supplied material to the second set of grooves in the lower/bottom side of the shim. After exiting the dispensing edge of the shim, the combined extrudate flowed 12.5 mm through the land region of the die and then were deposited vertically downward onto a 50 micron polyethylene terephthalate (PET) film and then cooled on a temperature-controlled chrome finish steel roll (20°C) at a line speed of 3.1 meter/minute. A photomicrograph of a cross-section of the film is shown in Figure 7 with the darker portions in the photomicrograph corresponding to the polyethylene.

**Example 2**

**[0058]** A coextruded film was prepared as in Example 1 except the flow rate of the polyethylene was 0.9 kg/hr. A photomicrograph of a cross-section of the film is shown in Figure 8 with the darker portions in the photomicrograph corresponding to the polyethylene.

**Example 3**

**[0059]** A coextruded film was prepared as in Example 2 except INFUSE D9507 (5 MI, available from Dow Chemical Co., Midland, MI)was used for the polyethylene layer. A photomicrograph of a cross-section of the film is shown in Figure 9 with the darker portions in the photomicrograph corresponding to the polyethylene.

**Example 4**

**[0060]** A coextruded film was prepared as in Example 2 except that the extrudate was deposited onto a PVC (vinyl) cast film in place of the PET film. A photomicrograph of a cross-section of the film is shown in Figure 10 with the darker portions in the photomicrograph corresponding to the polyethylene.

**[0061]** Embodiments of the invention have been discussed and described herein. The described embodiments are potentially amenable to various modifications and alterations by those of ordinary skill in the art without departing from the spirit and the scope of the invention.

**What is claimed is:**

1. An extrusion die for co-extruding a first molten polymeric material and a second molten polymeric material, the die comprising:

a first die portion;

a second die portion; and

a shim separating the first die portion and the second die portion, the shim having a first side and a second side, the first side of the shim forming a boundary of the first die portion and defining a first die cavity, the second side of the shim forming a boundary of the second die portion and defining a second die cavity, a dispensing edge comprising a plurality of first and second extrusion openings, a plurality of first feed channels connecting the first die cavity to the first extrusion openings along the dispensing edge, and a plurality of second feed channels connecting the second die cavity to the second extrusion openings along the dispensing edge, the first and second extrusion openings arranged along the dispensing edge to provide:

(a) an interfacial zone comprising portions of first extrusion openings disposed between portions of second extrusion openings,

(b) a first continuous zone comprising portions of the first extrusion openings arranged in side-by-side relation to each other, and

(c) a second continuous zone comprising portions of the second extrusion openings arranged in side-by-side relation to each other,

Wherein, the interfacial zone is disposed between the first continuous zone and the second continuous zone.

2. The die according to claim 1, wherein the shim comprises a metallic material.

3. The die according to claim 1, wherein the shim comprises a ceramic material

4. The die according to claim 1, wherein the first continuous zone along the dispensing edge is configured to provide an extrudate consisting essentially of the first molten polymeric material; the interfacial zone along the dispensing edge is

configured to provide an extrudate consisting essentially of both the first molten polymeric material and the second molten polymeric material; and the second continuous zone along the dispensing edge is configured to form an extrudate consisting essentially of the second molten polymeric material.

5. The die according to claim 1, wherein the interfacial zone along the dispensing edge is configured to provide an extrudate comprised of a structured interface or a microstructured interface between the first and second molten polymeric materials.

6. An extrusion system for the manufacture of a multilayered film, comprising:

The extrusion die according to any of claims 1-5;

A source of first molten polymeric material connected to the extrusion die to feed the first molten polymeric material into the first die cavity;

A source of second molten polymeric material connected to the extrusion die to feed the second molten polymeric material into the second die cavity;

Cooling apparatus positioned to receive a multilayered molten sheet from the extrusion die, the multilayered molten sheet comprising the first and second molten polymeric materials, the cooling apparatus being at a temperature sufficient to at least partially solidify the multilayered molten sheet.

7. The extrusion system according to claim 6 wherein the source of first molten polymeric material is a first extruder and the source of second molten polymeric material is a second extruder, the first and second extruders being selected from single screw extruders and twin screw extruders.

8. The extrusion system according to claim 6 wherein the cooling apparatus comprises a chill roll.

9. The extrusion system according to claim 6 wherein the cooling apparatus comprises a series of cooling rolls.

10. The extrusion system according to claim 6 wherein the cooling apparatus comprises a water bath.

11. A method of producing an extruded article, the method comprising:

providing an extrusion system according to any of claims 6-10;

feeding the first molten polymeric material from the source of first molten polymeric material into the first die cavity and through the plurality of first extrusion channels, the first molten polymeric material comprising a layer of pressure sensitive adhesive material having first and second major surfaces;

extruding the second molten polymeric material from the source of second molten polymeric material through the second die cavity and through the second extrusion channels, the second molten polymeric material comprising a polymer release material having first and second major surfaces;

the pressure sensitive adhesive material and the polymer release material exiting the extrusion die through the first and second extrusion openings along the dispensing edge of the die to provide a multilayered extrudate wherein the first major surface of the pressure sensitive adhesive overlays the first major surface of the polymer release material, the multilayered extrudate having a structured interface between the pressure sensitive adhesive and the polymer release material; and

cooling the multilayered extrudate to provide the extruded article in the form of a pressure sensitive adhesive layer having a release liner removably affixed to the adhesive layer.

12. The method according to claim 11 further comprising adding a backing material to the second major surface of the pressure sensitive adhesive material.

13. The method according to any of claims 11-12 further comprising adding a backing material to the second major surface of the polymer release material.

14. The method according to any of claims 11-13, wherein cooling the multilayered extrudate comprises contacting the extrudate on a chill roll.

15. The method according to any of claims 11-13, wherein cooling the multilayered extrudate comprises contacting the extrudate on a series of cooling rolls.

16. The method according to any of claims 11-13, wherein cooling the multilayered extrudate comprises contacting the extrudate with a water bath.

17. The method according to any of claims 11-16 , wherein the pressure sensitive adhesive is selected from the group consisting of acrylate, block copolymer, silicone and combinations thereof.

18. The method according to claim 17 wherein the block copolymer is a styrene-isoprene block copolymer.

19. The method according to claim 17 wherein the acrylate is the reaction product of acrylic acid and one or both of 2-ethylhexyl acrylate and isooctylacrylate.

20. The method according to claim 11-19, wherein the polymer release material is selected from the group consisting of polyolefin homo and copolymers, fluoropolymers, silicone polymers and combinations of two or more of the foregoing.

21. The method according to claim 20, wherein the polyolefin is selected from high density polyethylene, low density polyethylene, ultra-low density polyethylene and combinations thereof.

22. The method according to claim 20, wherein the polyolefin is selected from random or block copolymers of ethylene/propylene, ethylene/butene, ethylene/hexene, or ethylene/octene and combinations thereof.

23. An adhesive article made according to the method of any of claims 11-22.

24. An adhesive article, comprising:

An extruded pressure sensitive adhesive material layer having a first major surface and a second major surface, the second major surface having a microstructure provided by an extrusion die;

An extruded release liner comprising a polymeric material layer having a first major surface and a second major surface, the first major surface of the release liner being releasably affixed to the second major surface of the pressure sensitive adhesive material and the first major surface of the release liner having a microstructure complimentary to the microstructure of the second major surface of the pressure sensitive adhesive material layer;

Wherein, the microstructure on the first major surface of the extruded release liner will retain its microstructure when heated to the melting temperature of the first polymeric material.

25. The extruded article according to claim 24, wherein the extruded pressure sensitive adhesive material layer is selected from the group consisting of acrylate, block copolymer, and combinations thereof.

26. The extruded article according to claim 25 wherein the block copolymer is a styrene-isoprene block copolymer.

27. The extruded article according to claim 25 wherein the acrylate is the reaction product of acrylic acid and 2-ethylhexyl acrylate.

28. The method according to claim 25, wherein the polymer release material is selected from the group consisting of polyethylene, polypropylene, polyethylene terephthalate and combinations of two or more of the foregoing.

29. The method according to claim 28, wherein the polyethylene is selected from high density polyethylene, low density polyethylene, ultra-low density polyethylene, and combinations thereof.

30. The method according to claim 28, wherein the polyethylene is selected from random or block copolymers of ethylene/propylene, ethylene/butane, ethylene/hexene, or ethylene/octene.

31. The extruded article according to any of claims 24-30, further comprising a backing layer affixed to the second major surface of the pressure sensitive adhesive.

32. The extruded article according to any of claims 24-31 further comprising a backing layer affixed to the second major surface of the release liner.

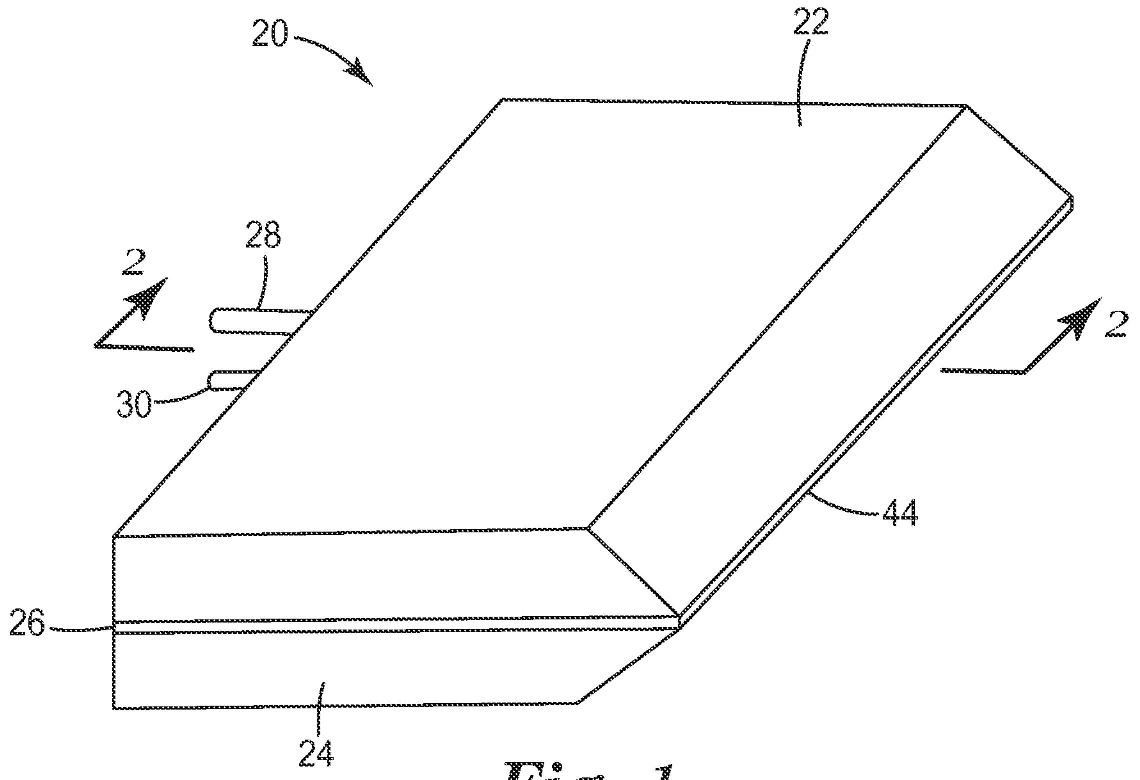


*Fig. 1*

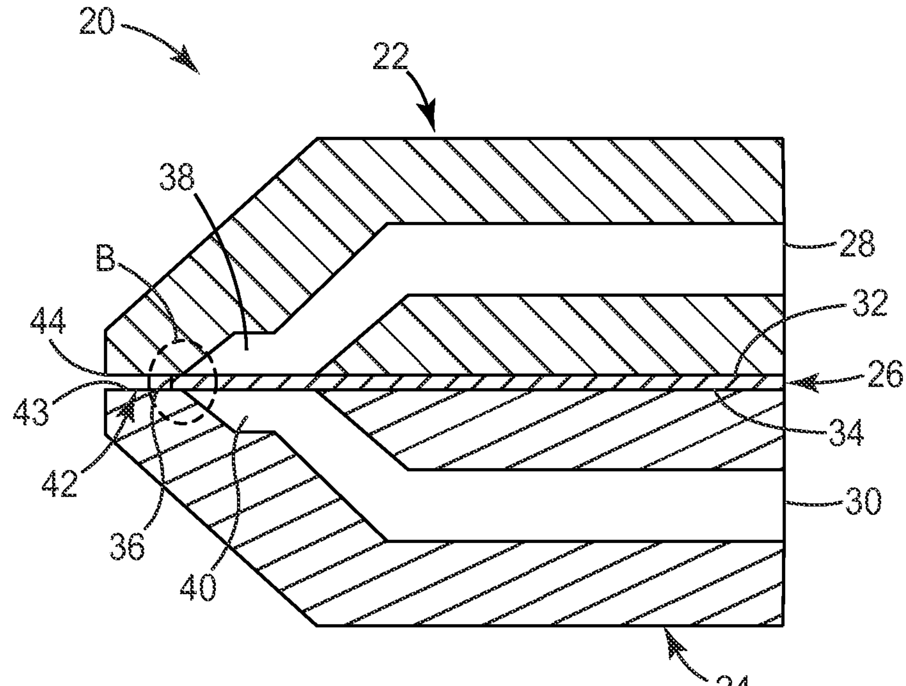


*Fig. 2*

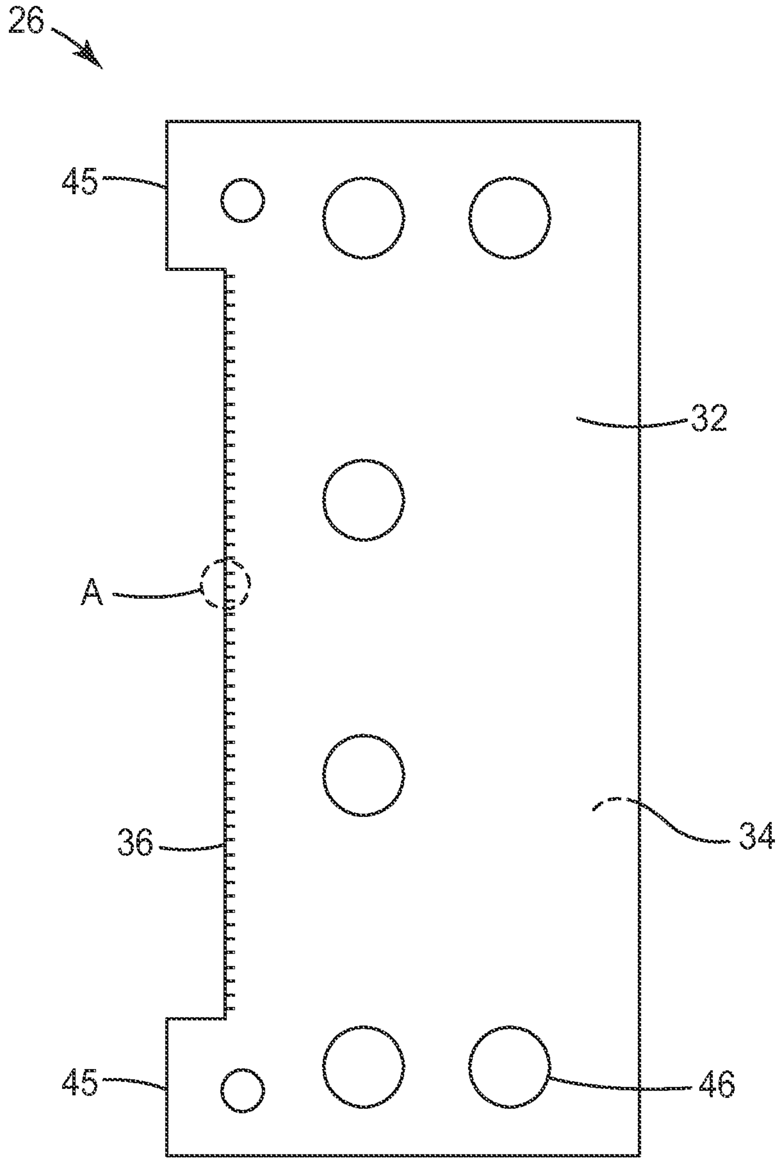


*Fig. 3*

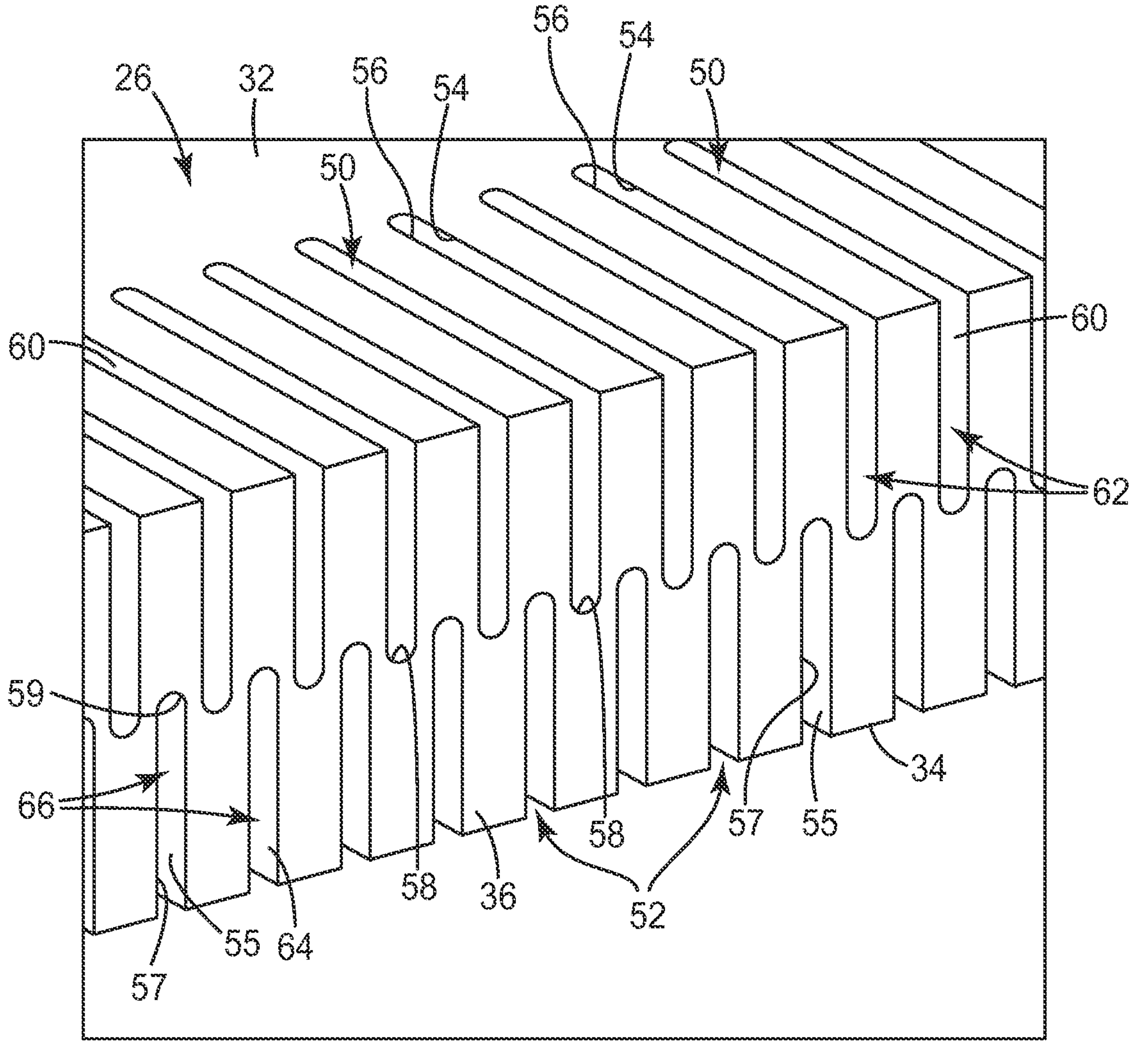
26
32
56
54
50
56
54
56
54
50
60
60
62
59
66
55
57
64
58
36
58
52
57
55
34

*Fig. 4*

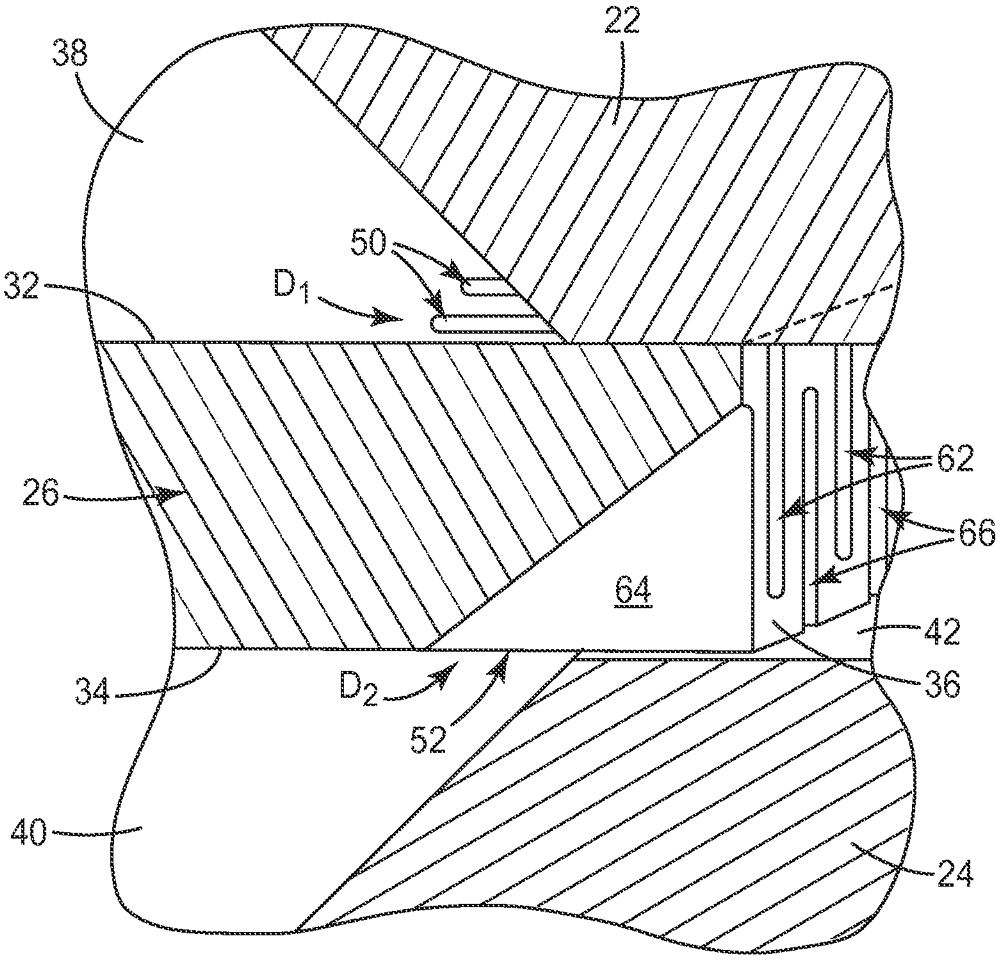


*Fig. 5*

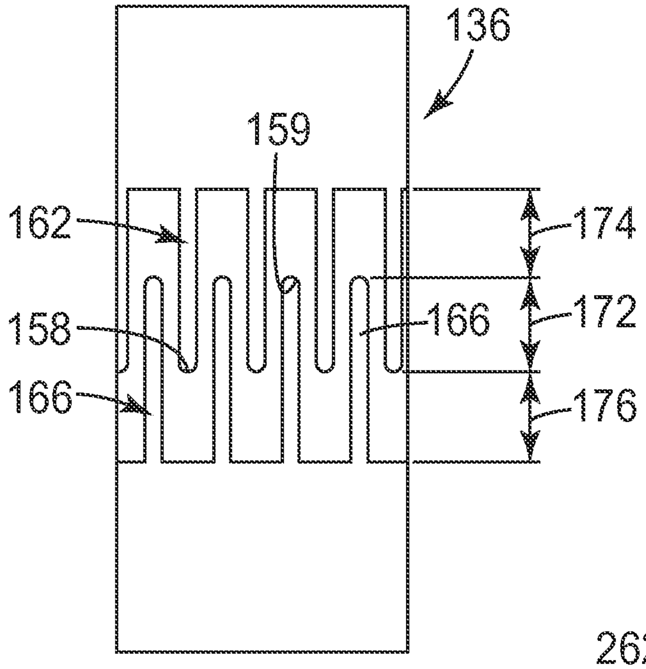


*Fig. 6A*

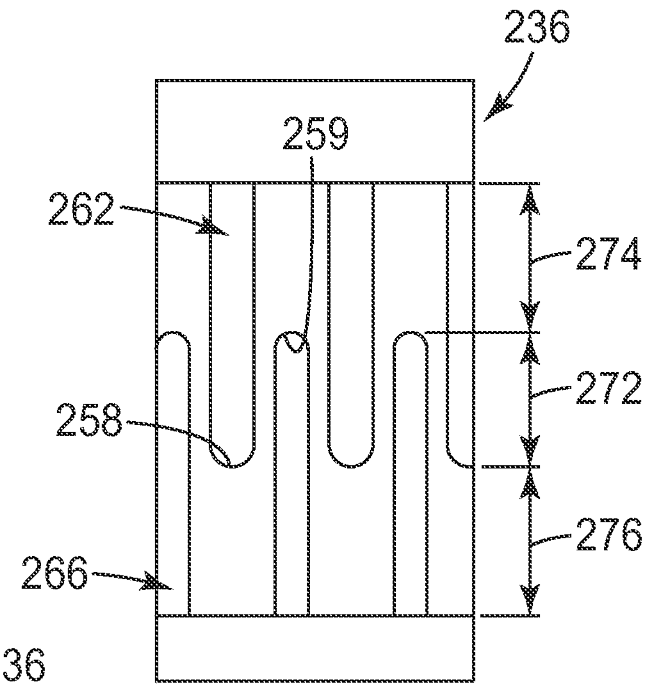


*Fig. 6B*

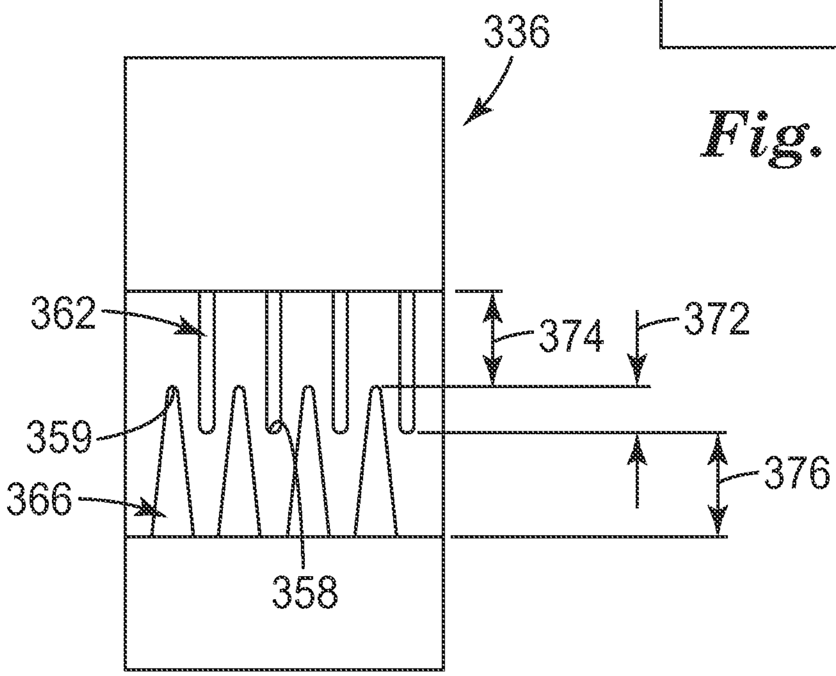


*Fig. 6C*

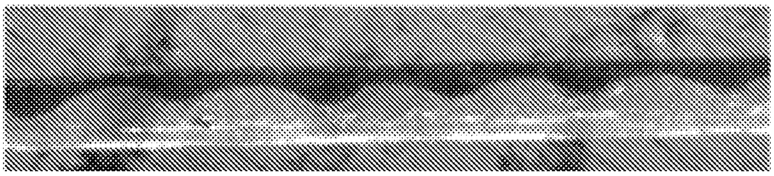

*Fig. 7*

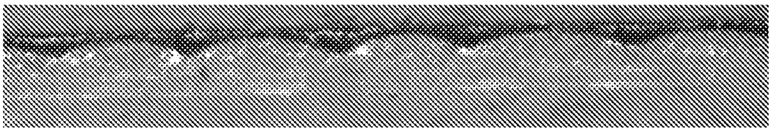

*Fig.8*

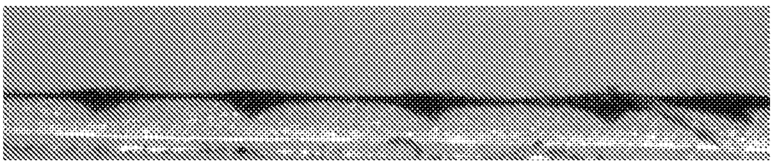

*Fig. 9*

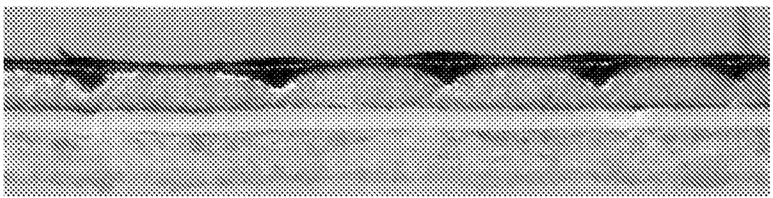

*Fig. 10*

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/060377

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. B29C47/06 B29C47/14 B29C47/58
ADD. C09J7/02 B29C47/88 B29C47/56

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 C09J

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>Y | US 4 426 344 A (DINTER PETER [DE] ET AL) 17 January 1984 (1984-01-17)<br>abstract<br>column 1, lines 40-68<br>column 2, line 54 - column 3, line 8<br>column 3, line 58 - column 4, line 3<br>column 5, line 39 - column 6, line 55<br>column 6, lines 56-68<br>column 7, lines 52-65<br>claims 1,11-17<br>figures 1-5<br>----- | 1-10<br>11-22 |

-/--

[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 |
|---|---|
| 2 May 2011 | 11/05/2011 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Ngwa, Walters |

2

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/060377

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br><br>Y | US 6 511 742 B1 (MUESSIG BERNHARD [DE] ET AL) 28 January 2003 (2003-01-28)<br>abstract<br>column 5, lines 43-54<br>column 6, lines 36-59<br>examples 1-3<br>claims 1-25<br>figures 1-2<br>----- | 23-32<br><br>11-22 |
| X<br><br>Y | US 2007/231571 A1 (LANE RICHARD [NL] ET AL) 4 October 2007 (2007-10-04)<br>abstract<br>paragraph [0017]<br>paragraph [0040] - paragraph [0050]<br>paragraph [0059]<br>paragraph [0109]<br>figures 9-11<br>----- | 23-32<br><br>11-22 |
| X | EP 0 160 857 A2 (CONTINENTAL GUMMI WERKE AG [DE]) 13 November 1985 (1985-11-13)<br>abstract<br>page 2, line 16 - page 3, line 13<br>claims 1-9<br>figures 1-7<br>----- | 1-5 |
| X | JP 49 108870 U (N.N.)<br>18 September 1974 (1974-09-18)<br>figures 1-3<br>----- | 1-5 |
| A | US 4 152 387 A (CLOEREN PETER [US])<br>1 May 1979 (1979-05-01)<br>abstract<br>column 4, lines 37-54<br>column 5, lines 44-55<br>column 10, lines 20-30<br>examples 1-2<br>figures 1-5<br>----- | 1-32 |

# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

International application No
PCT/US2010/060377

| Patent document cited in search report | | Publication date | Patent family member(s) | | | Publication date |
|---|---|---|---|---|---|---|
| US 4426344 | A | 17-01-1984 | DE | 3025564 | A1 | 04-02-1982 |
| | | | DK | 296481 | A | 06-01-1982 |
| | | | EP | 0043951 | A1 | 20-01-1982 |
| US 6511742 | B1 | 28-01-2003 | DE | 19955610 | A1 | 21-06-2001 |
| | | | EP | 1101808 | A2 | 23-05-2001 |
| | | | ES | 2208204 | T3 | 16-06-2004 |
| | | | JP | 2001152110 | A | 05-06-2001 |
| US 2007231571 | A1 | 04-10-2007 | CN | 101454416 | A | 10-06-2009 |
| | | | EP | 2001970 | A1 | 17-12-2008 |
| | | | JP | 2009532559 | T | 10-09-2009 |
| | | | WO | 2007126620 | A1 | 08-11-2007 |
| EP 0160857 | A2 | 13-11-1985 | DE | 3417452 | A1 | 14-11-1985 |
| | | | JP | 60253530 | A | 14-12-1985 |
| JP 49108870 | U | 18-09-1974 | JP | 53047514 | Y2 | 14-11-1978 |
| US 4152387 | A | 01-05-1979 | NONE | | | |